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A PROGRAM TO DEVELOP A HIGH-ENERGY DENSITY PRIMARY BATTERY WITH A MINI- MUM OF 200 WATT HOURS PER POUND OF TOTAL BATTERY WEIGHT

by

William E. Elliott, James R. Huff,
Robert W. Adler, Judith L. Jamrozy and Warren L. Towle

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-6015

FIFTH QUARTERLY REPORT

July 1 - September 30, 1965

A RESEARCH REPORT FROM
GLOBE-UNION INC.



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TABLE OF CONTENTS

	<u>Page</u>
List of Tables and Figures.....	ii
Summary.....	v
Introduction.....	vii
Abstract.....	viii
I. Overall Progress.....	1
II. Current Problems.....	21
III. Work to be Performed.....	22
IV. Test Results.....	IV-1
V. Distribution List.....	V-1

LIST OF TABLES AND FIGURES

		<u>Page</u>
Table I	Electrochemical Half-Cell Screening of Anodes.....	IV-1
Figure 1	Linearly Varying Potential Scans of a Lithium Anode in 1 Molal N-Phenyl N,N,N-Trimethylammonium Hexa- fluorophosphate-Dimethylformamide Electrolyte.....	IV-15
Table II	Electrochemical Half-Cell Screening of Cathodes.....	IV-17
Table III	Discharge of Cells Utilizing Dissolved Active Cathode Materials.....	IV-38
Table IV	Coulombic Efficiencies of Cathodes.....	IV-44
Figure 2	Constant Current Discharge for Cell A-2, Lithium vs. Cupric Fluoride Filter Pad Cathode in 1 Molal LiClO_4 -Propylene Carbonate Electrolyte.....	IV-48
Figure 3	% Theoretical Open Circuit Voltage (Full Cell) vs. % Theoretical Coulombs for Cupric Fluoride Filter Pad Cathodes vs. Lithium in LiClO_4 -Propylene Carbonate Electrolyte.....	IV-49
Figure 4	% Theoretical Open Circuit Voltage (Full Cell) vs. % Theoretical Coulombs for Cupric Fluoride Filter Pad Cathodes vs. Lithium in N-Phenyl N,N,N-Tri- methylammonium Hexafluorophosphate-Dimethylforma- mide Electrolyte.....	IV-50
Figure 5	% Theoretical Open Circuit Voltage (Full Cell) vs. % Theoretical Coulombs for Cupric Fluoride Filter Pad Cathodes vs. Magnesium in AlCl_3 -Acetonitrile Electrolyte.....	IV-51

LIST OF TABLES AND FIGURES (Continued)

Figure 6	Linearly Varying Potential Scans of Cupric Fluoride Filter Pad Cathodes in 1 Molal LiClO_4 -Propylene Carbonate Electrolyte.....	IV-52
Figure 7	Linearly Varying Potential Scans of Cupric Fluoride Filter Pad Cathodes in 1 Molal LiClO_4 -Propylene Carbonate and 1 Molal N-Phenyl N,N,N-Trimethylammonium Hexafluorophosphate-Dimethylformamide Electrolytes.....	IV-55
Figure 8	Linearly Varying Potential Scans of a Silver Oxide Cathode in 1 Molal N-Phenyl N,N,N-Trimethylammonium Hexafluorophosphate-Dimethylformamide Electrolyte....	IV-56
Table V	Data Given by Morehouse and Glicksman on Organic Cathode Materials in Aqueous Solutions.....	IV-58
Figure 9	Linearly Varying Potential Scans of 0.1 Molal N-Chlorosuccinimide in 1 Molal LiPF_6 -Dimethylformamide and 1 Molal LiPF_6 -N-Nitrosodimethylamine Electrolytes.....	IV-59
Figure 10	Linearly Varying Potential Scans of 0.1 Molal Meta-Dinitrobenzene in 1 Molal LiPF_6 -Dimethylformamide and 1 Molal LiPF_6 -N-Nitrosodimethylamine Electrolytes.....	IV-60
Figure 11	Linearly Varying Potential Scans of 0.1 Molal N-Chlorosuccinimide and 0.1 Molal Meta-Dinitrobenzene in 1 Molal LiPF_6 -Dimethylformamide Electrolyte.....	IV-61
Figure 12	Linearly Varying Potential Scans of 0.1 Molal 4-Nitrosophenol and 0.1 Molal 2,4-Dinitrophenol in 1 Molal LiPF_6 -Dimethylformamide Electrolyte.....	IV-62
Figure 13	Linearly Varying Potential Scans of 1 Molal Picric Acid in 1 Molal N-Phenyl N,N,N-Trimethylammonium Hexafluorophosphate-Dimethylformamide Electrolyte and 0.1 Molal Para-Quinonedioxime in 1 Molal LiPF_6 -Dimethylformamide.....	IV-63

LIST OF TABLES AND FIGURES (Continued)

Table VI	Discharge of Cells Utilizing m-Dinitrobenzene as the Active Organic Cathode Material.....	IV-64
Table VII	Specifications for Speer Carbons Used in Electro- chemical Testing of Dissolved Active Cathode Materials.....	IV-70
Table VIII	Discharge of Cells Utilizing an Ion Exchange Membrane Separator.....	IV-71
Table IX	Chemical Stability of Anode Materials in Electrolyte Solutions.....	IV-74
Table X	Distillation and Testing of Solvents Employed in Electrolytic Solutions.....	IV-83
Table XI	Electrochemical Half-Cell Screening of Anodes in Purified Solvents.....	IV-88

SUMMARY

Thirteen new anode-electrolyte combinations were studied in the continuation of a screening program designed to select those systems which are most promising for future development of high energy batteries. Of these, one system could sustain discharge at 100 ma/cm^2 without excessive polarization and six others could sustain at least 10 ma/cm^2 . Linearly varying potential studies and coulombic efficiency studies were made of anode systems which had exhibited promising characteristics in preliminary studies.

Cathodes were prepared for use in half-cell screening tests from cuprous chloride, cupric chloride, cupric oxychloride, cupric fluoride, manganese dioxide, silver fluoride, silver difluoride, and silver oxide. Various fabrication techniques were used in an effort to improve electrode conductivity. These included the addition of conducting substances to the electrode, attempts to improve electrode porosity, and use of cathode materials which are themselves conductive or can be made conductive by doping. Arsenic trifluoride and m-dinitrobenzene dissolved cathodes were also investigated.

In addition to preliminary half-cell screening tests, further attempts have been made to characterize electrochemical reactions at the cathode. Coulombic efficiency studies were made of cupric fluoride, lead dioxide, silver difluoride, and silver oxide electrodes in various electrolytes. Linearly varying potential studies were made of various cathode materials: cupric fluoride, silver oxide, and organic compounds.

An ion exchange membrane was tested for use as a separator, particularly when dissolved cathodes are employed, to prevent transfer of cations from the active cathode material.

SUMMARY (Continued)

Chemical stability tests were conducted for electrode materials in various electrolytes. Vacuum distillation of solvents used in electrolytic solutions was continued in an attempt to free solvents of impurities, particularly water, and to insure reproducibility of results in electrochemical tests.

INTRODUCTION

The objective of this research is to develop a primary battery with an energy density of at least 200 watt-hours per pound of total battery weight.

Preliminary electrochemical evaluations of calcium, lithium and magnesium anodes in various electrolytes have been virtually completed. Several promising combinations have been selected for a more thorough investigation.

Efforts have been made to improve the electrochemical characteristics of cupric fluoride cathodes. Concurrently, consideration has been given to possible approaches for eliminating some of the difficulties associated with conventional techniques of cathode fabrication. In addition, other cathode materials with high theoretical energy densities have been investigated.

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ABSTRACT

11247

Electrochemical half-cell screening of thirteen anode-electrolyte combinations was carried out and coulombic efficiency and linearly varying potential studies were made for several anode systems. Cathodes made from Cu_2Cl_2 , CuCl_2 , $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 4\text{H}_2\text{O}$, CuF_2 , MnO_2 , AgF , AgF_2 and AgO were tested for electrochemical capabilities. Arsenic trifluoride and m-dinitrobenzene dissolved cathodes were also tested. Coulombic efficiency and linearly varying potential studies were made of several of the above cathodes. Linearly varying potential studies were also made of organic cathode materials under investigation.

Three cells were discharged using an ion exchange membrane separator to inhibit transfer of cations of the cathode material. Compatibility tests involving electrode materials were completed in several electrolytes. Distillation and characterization of solvents used in electrolytic solutions was continued. Electrochemical half-cell screening tests were conducted in two of these solvents.

Author

I. OVERALL PROGRESS

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Progress during the Fifth Quarter encompassed work in the following areas:

1. Electrochemical half-cell screening of anodes.
2. Coulombic efficiency studies of anodes.
3. Linearly varying potential studies of anodes.
4. Development of cathodes. Fabrication and electrochemical studies.
5. Discharge of cells utilizing dissolved active cathode materials.
6. Coulombic efficiency studies of cathodes.
7. Linearly varying potential studies of cathodes.
8. Investigation of the feasibility of utilizing active organic cathode materials.
9. Discharge of cells utilizing an ion exchange membrane separator.
10. Chemical stability of electrode materials in electrolyte solutions.
11. Distillation and testing of solvents employed in electrolytic solutions.
12. Electrochemical half-cell screening of anodes in purified solvents.

Experimental Approaches and Results.

1. Electrochemical Half-Cell Screening of Anodes.

The procedure for rapid, preliminary evaluation of prospective anode-electrolyte combinations on the basis of polarization measurements was described in detail in the Third Quarterly Report. This work was continued during the fifth quarter to include thirteen systems which had not been studied previously. Of the anode systems investigated, only one could sustain a 100 ma/cm^2 discharge. This system consisted of a lithium anode in a LiPF_6 -N-nitrosodimethylamine (NDA) electrolyte. Six anode-electrolyte combinations were qualified as being capable of discharge at a current density of at least 10 ma/cm^2 . The remaining

systems exhibited excessive polarization at currents of 10 ma/cm² and were classified as 1, 0.1, or less than 0.1 ma/cm² capability systems.

Of particular interest was a lithium anode in tri-n-propylammonium hexafluoroarsenate-dimethylformamide (DMF). This system had previously been classified as capable of sustaining 100 ma/cm². However, vigorous gas evolution had occurred during the half-cell test. A 1 molal solution of tri-n-propylammonium hexafluoroarsenate-DMF was pretreated with lithium until gas evolution ceased and was then used in a lithium anode screening test. The pretreated system could still maintain a current density of at least 10 ma/cm² and gas evolution was not observed. The pretreated electrolyte had a conductivity of $1.65 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ as compared to a value of $2.20 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ for the untreated electrolyte.

Further investigation has been made of the lithium-morpholinium hexafluorophosphate-N-nitrosodimethylamine system in which the electrolyte was pretreated with lithium until gas evolution ceased. It was postulated that treatment of the morpholinium hexafluorophosphate-NDA solution with lithium might result in the formation of LiPF₆ and morpholine. During this quarter, a lithium anode was tested in a LiPF₆, morpholine-NDA electrolyte. The specific conductance of this electrolyte was $1.85 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ compared to a value of $1.81 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ for the morpholinium hexafluorophosphate-NDA solution pre-treated with lithium. (The specific conductance of 1 m LiPF₆-NDA is $2.40 \times 10^{-2} \text{ ohm}^{-2} \text{ cm}^{-1}$.) In addition to the similarity in specific conductivity for the two solutions, half-cell screening of a lithium anode in LiPF₆, morpholine-NDA and pre-treated morpholinium hexafluorophosphate-NDA yielded similar voltages at various current densities. However, during the discharge of the LiPF₆, morpholine-NDA half-cell, continuous gassing occurred at the lithium anode. This did not occur in the pre-treated morpholinium hexafluorophosphate-NDA system. Further

evaluation will have to be made to determine conclusively whether the reaction of lithium with morpholinium hexafluorophosphate-NDA does produce LiPF_6 and morpholine.

The data for the electrochemical half-cell screening of anodes is given in Table I, p. IV-1 through IV-14.

2. Coulombic Efficiency Studies of Anodes.

One coulombic efficiency test was performed according to the procedure described in the Fourth Quarterly Report. The coulombic efficiency of a magnesium anode (0.10 g) in 1 molal AlCl_3 -acetonitrile was determined using a silver-silver chloride counter electrode. The cell was allowed to discharge at a constant current of 50 ma*. The anode maintained a voltage of -1.4 V during the discharge and an efficiency of 82% was achieved. The discharge ended when the magnesium, which had partially disintegrated, separated from the lead. Because electrical contact was broken, a coulombic efficiency of 82% is a conservative estimate.

3. Linearly Varying Potential Studies of Anodes.

Linearly varying potential studies, as described in the Fourth Quarterly Report, were carried out with a lithium anode in a 1 molal N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolyte. Some of the results of these tests are depicted in Figures 1a and b, pages IV-15 and IV-16. The curves indicate that only one reaction takes place in the voltage range examined, i.e., -3.2 to -1.0 volts vs. Ag/AgCl. The reaction does not appear to be reversible. However, scan 4, p. IV-16, is typical of a steady state reached after several scans between -3.2 and -1.0 volts and the limiting current is 310 ma/cm². At the more negative voltages, the currents obtained are also in accord with the results obtained during screening experiments in this electrolyte.

* The original current density was 50 ma/cm² but surface area decreased during the test while the current remained 50 ma.

4. Development of Cathodes. Fabrication and Electrochemical Studies.

During the fifth quarter, greater emphasis has been placed on fabrication of cathodes. A variety of materials and fabrication techniques have been used in an effort to solve the problem of poor electrode conductivity. The main approaches to this problem have been:

- 1) Inclusion of a conducting substance in the cathode mix.
- 2) Inclusion of a volatile substance in the cathode mix which can be sublimed to improve cathode porosity.
- 3) Inclusion of a small amount of the solute, which is employed in the electrolyte, in the cathode mix. When the cathode is immersed, the solute will dissolve in the electrolyte, leaving the cathode in a porous condition.
- 4) Use of cathode materials which are themselves conductive or can be made conductive by doping.

Cuprous and cupric chloride cathodes were prepared by dipping a metal matrix into the molten salt and cooling. A cathode was also prepared in this manner from a mixture of cupric chloride (25 weight %) and cuprous chloride (75 weight %). The pure cuprous and cupric chloride cathodes could both sustain a current density of at least 10 ma/cm² with polarization of less than 0.5 volts from the open circuit voltage. The cathode prepared from a mixture of cuprous and cupric chloride performed similarly to a pure cupric chloride electrode and both of these were superior to the pure cuprous chloride cathode.

A cupric oxychloride cathode was also prepared from a mixture of approximately 75 mole % CuO and 25 mole % CuCl₂·2H₂O. It was postulated that this mixture of compounds might exhibit greater conductivity than pure CuCl₂. The cathode retained its mechanical integrity during discharge. The cupric oxychloride cathode was tested in 1 molal N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-DMF and could sustain a current density of 1 ma/cm² with a 0.21 V drop from the open circuit value of +0.13 V. It polarized appreciably to -1.78 V during the 5 ma/cm² discharge.

Various cupric fluoride cathodes were fabricated in an attempt to improve conductivity. The first of these was prepared from a mixture of cupric fluoride (92 weight %), Solka-Floc binder (5 weight %), and Shawinigan acetylene black (3 weight %). The mixture was dry-pressed on a silver grid at a pressure of 10,000 lb./cm². This cathode was tested in order to compare acetylene black as a conductive additive with other forms of carbon used previously. However, poor adhesion of the cathode pellet to the silver matrix caused polarization of more than 1 V during the 5 ma/cm² discharge and prevented an evaluation from being made.

Two cupric fluoride cathodes were prepared from a mixture of cupric fluoride, Solka-Floc, carbon black, and phenol. The phenol was sublimed at 140°C in an argon atmosphere. However, this attempt to increase the porosity of the dry-pressed pellet resulted in poor adhesion of the cathode materials to the support grid. In both cases, the portion of the electrode facing the counter electrode separated from the support grid during the 1 ma/cm² discharge and severe polarization resulted.

The most promising method of fabricating cupric fluoride cathodes during this quarter proved to be the filter pad method developed by Livingston Electronic Corporation under NASA contract NAS3-7632. The fabrication of these electrodes involves formation of a heptane slurry of cupric fluoride, graphite, and filter paper pulp. The slurry is filtered on a Büchner funnel and pressed on expanded nickel metal. The cupric fluoride filter pad cathode exhibited a potential varying between -0.28 and -0.35 V (vs. Ag/AgCl) at a current density of 10 ma/cm² over a five minute discharge period, compared to an open circuit value of +0.67 V. Electrodes of this type were used for coulombic efficiency determinations and linearly varying potential studies.

Attempts were also made to improve the conductivity of cupric fluoride electrodes by doping with cobalt trifluoride, ferric fluoride, and lithium fluoride. Two techniques were used. First, the salts were melted together, cooled, pulverized, mixed with a Solka-Floc binder and pressed on a metal matrix. The second method involved co-precipitating the two salts from a pyridine solution, vacuum drying the precipitate, mixing the dried precipitate with a Solka-Floc binder, and dry-pressing the resulting substance on a metal matrix.

Doped cupric fluoride cathodes prepared according to the first method polarized more than 1 V from the open circuit potentials at a 1 ma/cm² discharge rate. Electrodes prepared by the co-precipitation method also exhibited poor electrochemical performance. However, full evaluation of the co-precipitation method could not be made because the salts used were only partially soluble in pyridine. Further attempts to dope cathodes using the co-precipitation method in more appropriate solvents are planned for the future.

A number of cathodes were prepared from silver difluoride, silver fluoride, silver oxide, and silver fluoride containing small amounts of silver oxide. Silver difluoride electrodes prepared from a mixture of AgF₂ (95 weight %) and Solka-Floc binder (5 weight %) dry-pressed on an expanded silver matrix at 15,000 lb/cm² were tested in 1 molal AlCl₃-acetonitrile using a magnesium counter electrode. These electrodes could sustain discharge currents of at least 25 ma/cm² with less than 0.9 V polarization from an open circuit potential of +0.22 V.

Silver oxide electrodes prepared by dry-pressing AgO on a silver metal matrix were tested in KAsF₆-dimethylformamide and N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolytes using a lithium counter electrode. The AgO electrodes could sustain at least 5 ma/cm² with less than 1 V polarization from the open circuit potential. A silver oxide cathode was also prepared from a mixture of AgO (95 weight %) and Solka-Floc binder (5 weight %)

dry-pressed on a silver metal matrix at 20,000 lb/cm² and was tested in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-DMF using a lithium counter electrode. This cathode had an open circuit potential of +0.60 V and had polarized to -0.88 V by the end of the 25 ma/cm² discharge. The half-cell was allowed to discharge spontaneously at 50, 60 and 80 ma/cm² and maintained voltages of -1.10, -1.42 and -1.78 respectively. X-ray diffraction analysis of the electrode after the discharges showed 100% conversion to silver metal on the surface.

A silver fluoride cathode discharged in MgCl₂-N-nitrosodimethylamine using a lithium counter electrode exhibited excessive polarization at 1 ma/cm². Silver fluoride electrodes containing small amounts of silver oxide and discharged in the same electrolyte showed little improvement. However, when the silver fluoride-silver oxide electrodes were discharged in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-DMF instead of MgCl₂-NDA, marked improvement was observed. Silver fluoride-silver oxide cathodes in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-DMF could sustain discharges of 5 ma/cm² with only a 0.5 V drop from the open circuit potential. Since pure silver fluoride cathodes have not been tested in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-DMF yet, no conclusions can be made about the effect of doping silver fluoride with silver oxide at this time.

One manganese dioxide cathode was prepared using phenol to increase porosity. This cathode performed poorly in an electrochemical half-cell test, polarizing to -0.90 V from an open circuit value of -0.01 during the 0.1 ma/cm² discharge.

The data for the fabrication and electrochemical half-cell screening of cathodes are presented in Table II, p. IV-17 through IV-37.

5. Discharge of Cells Utilizing Dissolved Active Cathode Materials.

Investigation of soluble cathode materials initiated during the fourth quarterly reporting period has been continued. The use of cathodes of this kind eliminates certain problems of fabrication, such as establishing contact between the active cathode material and a conducting species. The main problem in utilizing this type of material is that of preventing

attack of the negative electrode by the soluble cathode material. In the tests performed during this period, liquid arsenic trifluoride, which has a theoretical energy density of greater than 700 watt-hours per pound when coupled with lithium, was utilized as the active cathode material. The arsenic trifluoride was placed in a porous carbon container to reduce its rate of transfer to the lithium anode.

Two cells composed of a lithium anode, arsenic trifluoride cathode, and N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolyte were allowed to discharge at a constant current of 10 ma. A variable resistor, described in the Fourth Quarterly Report, was used to maintain a constant current. The porous carbon container used for the arsenic trifluoride was platinized in the first of these cells and unplatinized in the second. Platinizing the carbon container had no apparent effect on performance. A cell was also discharged utilizing a porous carbon container identical to those used in the other cells, but containing no active cathode material. The results showed that the carbon container does not contribute to any observable degree to the electrochemical activity attributed to the active cathode material.

The lithium-arsenic trifluoride cells could maintain voltages of approximately two volts for at least 19 hours at a discharge current of 10 ma. The geometric area of the carbon cup exposed to the electrolyte was approximately 8 cm². The lithium was slowly attacked, indicating that if separation could be effected, the cell would be operable at currents of at least 10 ma. Ion exchange membranes are now being investigated for use in this type of cell. A suitable ion exchange membrane could effect separation of the electrode components and at the same time might allow the necessary transport of conducting ions.

Data for the above cells are presented in Table III, pages IV-38 through IV-43.

6. Coulombic Efficiency Studies of Cathodes.

Coulombic efficiency determinations were made for cupric fluoride filter pad cathodes, a cupric fluoride filter pad cathode containing LiClO_4 , a lead dioxide cathode, silver difluoride cathodes, and a silver oxide cathode according to the procedure described in the Fourth Quarterly Report. The cells were discharged at constant currents maintained by a transistorized variable resistor apparatus. The cathodes used had an area of 1 cm^2 . The electrolytes used were 1 molal in concentration. Polypropylene containers having an average weight of 5.3 g were employed in all cases and the electrodes were placed 2 cm apart. A silver-silver chloride reference electrode was used in these cells. The test cut-off voltage was 0.2V (full cell); this limit was used since constant current could not be maintained by the variable resistor below this point. In most cells, the discharge current was recorded in order to correct for variations in the constant current apparatus. These variations occur because the low currents are very near the control limits of the apparatus.

Coulombic efficiency determinations were made for cupric fluoride filter pad cathodes in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide, AlCl_3 -acetonitrile, and LiClO_4 -propylene carbonate. The cupric fluoride filter pad cathodes discharged in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate electrolytes yielded the greatest efficiencies. The plots of % theoretical open circuit voltage (full cell) vs. % theoretical coulombs in Figure 4, p. IV-50, show that there are two steps in the discharge. The first step is attributed to the reduction of cupric fluoride while the second is assigned to decomposition of the electrolyte. Two of these cells, discharged at 1.46 and 8.6 ma/cm^2 , yielded efficiencies in excess of 100%. This indicates that the reduction of some component of the electrolyte may be contributing to the overall coulombic output of the cell. A similar cell discharged at 5 ma/cm^2 yielded an efficiency of only 60.5%. This discrepancy can be attributed to the fact that not enough anode material was present in the latter cell and the length of discharge was governed by the Li electrode. The discharge was also terminated before the cut-off voltage of 0.2 V.

Cells consisting of a cupric fluoride filter pad cathode, a lithium anode, and a LiClO_4 -propylene carbonate electrolyte yielded greater efficiencies than those consisting of the same cathode, a magnesium anode, and an AlCl_3 -acetonitrile electrolyte. As can be seen from the tables below, greater efficiencies were obtained at lower discharge current rates.

CuF_2 vs. Li in LiClO_4 -Propylene Carbonate

<u>Cell No.</u>	<u>Discharge Current</u>	<u>% Efficiency</u>
A-1	1.5 ma	50.0
A-2	5 ma	23.0
A-3	10.6 ma	11.9

CuF_2 vs. Mg in AlCl_3 -Acetonitrile

A-7	1.4 ma	*24.1
A-8	5 ma	13.2
A-9	10.8 ma	4.3

Anode, cathode, and cell voltage as a function of time for cell A-2 are shown in Figure 2, p. IV-48. The full cell and cathode curves indicate the possibility of two different voltage plateaus in the cathode discharge. This behavior was typical of the cells consisting of a cupric fluoride filter pad cathode, lithium anode, and LiClO_4 -propylene carbonate electrolyte.

Since coulombic efficiency tests in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide have presented the possibility of reduction of a component of the electrolyte, graphs

* Discharge was halted before the cut-off cell voltage of 0.2 V was reached because of erratic cathode voltage readings. The efficiency calculated is therefore lower than the value which would have been obtained if the cell had been allowed to discharge to the usual cut-off point.

of % theoretical open circuit voltage (full cell) vs. % theoretical coulombs have been made for the nine cupric fluoride filter pad cathodes tested and are presented on p. IV-49 through IV-51. These curves indicate voltages at which reduction of materials other than cupric fluoride may be taking place.

Coulombic efficiency studies were also made for a cupric fluoride filter pad cathode containing LiClO_4 . The cathode was discharged at an average current density of 1.87 ma/cm^2 in a LiClO_4 -propylene carbonate electrolyte using a lithium anode. It yielded an efficiency of 31.8% compared to 50.0% for a cupric fluoride filter pad cathode discharged at 1.5 ma/cm^2 but not containing LiClO_4 .

A full cell consisting of a lithium anode, a lead dioxide cathode, and a magnesium chloride-N-nitrosodimethylamine electrolyte was discharged at 10 ma/cm^2 . Only 5.6% utilization of the lead dioxide was achieved, presuming that PbO_2 was reduced to PbO .

Silver difluoride electrodes yielded efficiencies of 24.1% and 29.7% at discharges of 1.7 and 1.9 ma/cm^2 respectively. An AlCl_3 -acetonitrile electrolyte and magnesium counter electrode were employed in both tests.

A silver oxide cathode discharged at 9.1 ma/cm^2 in N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide with a lithium counter electrode had an efficiency of 89.4%. The major portion of this discharge was at voltages where electrolyte decomposition takes place and, possibly, only a small portion of the coulombs obtained are due to AgO reduction.

The data for the coulombic efficiency tests are listed in Table IV, p. IV-44 through IV-47. X-ray analyses of most of the cathodes after discharge are included.

7. Linearly Varying Potential Scans of Cathodes.

Linearly varying potential studies, as described in the Fourth Quarterly Report, were carried out with cupric fluoride filter pad cathodes in 1 molal LiClO_4 -propylene carbonate and 1 molal N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolytes. Some of the results of these tests are depicted in Figures 6a, b, c, and d and in Figure 7, pages IV-52 through IV-55. The curves all indicate that only one reaction takes place in the voltage range examined, i.e., +1.5 to -1.5 volts vs. Ag/AgCl. The reaction is not reversible in this region; however, some amount of recharging does take place as indicated by the increase in peak current after scanning to more positive potentials, e.g., compare scan 3 and scan 4, Figure 6c, p. IV-53.

The series of runs in LiClO_4 -propylene carbonate was made without any pauses except for the one minute hold at -0.5 V (vs. Ag/AgCl) during scan 6, p. IV-54, and serves to illustrate the effect of varying the initial potential and point of reversal of voltage integration on peak currents and curve shapes. Figure 7, p. IV-55, shows a comparison of scans in two different electrolytes. The difference in position and shape of the current maxima is quite marked. It is interesting to note that, as given in Table IV, pages IV-46 and IV-47, the coulombic discharge efficiency was higher for the test using N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-DMF as the electrolyte.

Studies were also made of a AgO cathode in a 1 molal N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolyte. Selected scans are shown in Figures 8a and b, pages IV-56 and IV-57. Scans 1 and 6, p. IV-56, were taken from a consecutive series of runs between +0.60 and -1.0 volts vs. Ag/AgCl. The plateau between -0.4 and -0.6 volts was quite reproducible. In general, these curves only showed the one plateau and exhibited some amount of recharging, e.g., scan 15, p. IV-57, shows a definite increase in current after a scan to more positive voltages.

8. Investigation of the Feasibility of Utilizing Active Organic Cathode Materials.

Certain organic compounds show promise as soluble cathode materials owing to their low equivalent weight and their high solubility in the solvents now being employed in electrolytic solutions. For example, m-dinitrobenzene has an equivalent weight of 14 if both nitro groups are reduced to amino groups. From an investigation of the work done by Morehouse and Glicksman in aqueous electrolytes, a number of compounds have been selected for study. These compounds were chosen according to the voltages they exhibited during discharge and according to their efficiency in amp-minutes/gram. Data for these compounds can be found in Table V, page IV-58. In addition to these compounds, picric acid is being investigated.

Linearly varying potential studies were made of six organic cathode materials. The results of these tests are depicted in Figures 9 through 13, pages IV-59 through IV-63. On the basis of these data, further quantitative tests will be made with meta-dinitrobenzene (MDB), 2,4-dinitrophenol and N-chlorosuccinimide (NCS). The two nitro compounds gave high currents and the chloro compound had its current maximum at the most positive voltage. In addition, the 2,4-dinitrophenol appears to be reversible in the voltage range examined. Figures 9 and 10 demonstrate the effect of solvent on the position of the current maximum for MDB and NCS. MDB shows only a slight shift in potential between DMF and NDA; however, the change is much more pronounced for NCS. This result serves to emphasize the necessity of testing active materials in more than one electrolyte.

Three full cells were discharged utilizing m-dinitrobenzene dissolved in acetonitrile as the active cathode material. Magnesium anodes and a morpholinium hexafluorophosphate-acetonitrile electrolyte were employed. Three types of Speer carbon of varying porosity were used as containers for the soluble cathode materials. The discharge current was varied in order to determine the effect of

porosity on the voltages which the cathodes could sustain at different current densities. Less polarization was observed for the cells in which the HP-15 and HP-20 Speer carbons were used. (HP-10 Speer carbon was more porous than the HP-15 and HP-20 Speer carbons.)

A full cell was also discharged using solid m-dinitrobenzene as the active cathode material. A lithium anode and LiPF_6 -N-nitrosodimethylamine electrolyte were employed. Irregularities in voltage readings for this cell may indicate problems of dissolution and diffusion which were not observed when the m-dinitrobenzene was in solution. The change to the inorganic solute also seemed to affect the cathode. In the cells containing a morpholinium hexafluorophosphate-acetonitrile electrolyte, a yellow solid formed on the outside of the porous carbon container. This was not observed in the cell containing a LiPF_6 -N-nitrosodimethylamine electrolyte.

Electrochemical data for the m-dinitrobenzene cells are given in Table VI, pages IV-64 through IV-69. Porosity data for the Speer carbons used as soluble cathode containers are presented in Table VII, page IV-70.

9. Discharge of Cells Utilizing an Ion Exchange Membrane Separator.

An anion exchange membrane (E-5451- $\frac{1}{2}$, Ionics, Inc.) was tested in three cells for possible use as a separating material. The first cell consisted of a lithium anode, a cuprous-cupric chloride cathode and a LiClO_4 -propylene carbonate electrolyte. The potential drop across the membrane at a discharge current of 5 ma, as measured by a Ag/AgCl reference electrode in the anolyte and one in the catholyte, ranged from +0.84V to +1.08V. This resulted in a cell voltage of less than 1V. At a discharge current of 2 ma, the potential drop was +0.53V and cell voltage increased to 2V.

In the second cell, using the same type of membrane, a lithium anode and a $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -propylene carbonate soluble cathode were used. A

copper screen was used as the cathodic current collector. The anolyte was LiClO_4 -propylene carbonate. In this cell, a deposit formed at the cathode side of the membrane, possibly copper metal or a copper salt. Cell voltage dropped rapidly to less than 1V at a discharge current of 5 ma. The poor performance of this cell may have been due to the absence of a supporting electrolyte in the cathode compartment.

In the third cell a saturated solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1 molal N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide was employed as the active cathode material and copper metal served as the cathodic current collector. A lithium anode and N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide electrolyte were used. The drop in potential across the membrane in this cell was less than in the other two cells but an adequate evaluation could not be made due to leakage of the catholyte into the anode compartment. This leakage resulted from improper sealing of the membrane into position and did not occur through the membrane itself.

In general, it can be stated that the ion exchange membrane tested was unsatisfactory. Future work will include experimentation with different types of ion exchange membranes and also with filter paper and porous plastic separators.

The results for the discharge of cells utilizing an ion exchange membrane are presented in Table VIII, p. IV-71 through IV-73.

10. Chemical Stability of Electrode Materials in Electrolyte Solutions.

The procedure adopted for stability determinations at room temperature, described in the Third Quarterly Report, was again used. Calcium, lithium, and magnesium were tested over a period of two weeks in fifteen electrolytes. The results are given in Table IX, p. IV-74 through IV-82. It has been found that certain anode materials are stable in electrolyte solutions after an initial exposure period. Half-cell screening tests have already been completed in electrolytes which were pretreated with the anode material and filtered. In the

future, stability tests in these pretreated electrolytes will be conducted.

Stability tests of less than twenty-four hours were completed for silver oxide, now being investigated as a cathode material. The results are listed below:

<u>Solvent</u>	<u>Solute</u>	<u>Observations</u>
Acetonitrile (AN)	None	No change.
Dimethylformamide (DMF)	None	Solution changed from colorless to dark brown.
N-Nitrosodimethylamine (NDA)	None	No change.
AN	AlCl_3	Reacts with gassing to form a white solid.
AN	KPF_6	Slight gassing.
AN	LiPF_6	Reacts with gassing to form a white solid.
DMF	KAsF_6	Solution changed from colorless to light brown.

11. Distillation and Testing of Solvents Employed in Electrolytic Solutions.

The distillation of solvents used in electrolytic solutions has been continued in an effort to remove impurities (especially water, which might have a deleterious effect on the anode materials being used). It is also hoped that distillation of these solvents will assure greater reproducibility of results in electrochemical tests. The distillation procedure and method of solvent characterization were described in detail in the Fourth Quarterly Report.

During this period, propylene carbonate and N-nitrosodimethylamine were fractionally distilled at low pressures. The drying agents used were calcium hydride and molecular sieves respectively. Vapor pressure and vapor temperature ranges for each 100 ml fraction collected are given in Table X, p. IV-84.

Solvent characterization thus far has consisted of measuring specific conductivity and refractive index for the distilled solvent fractions at regular intervals during a twenty-four week period. The solvent fractions are stored in a dry argon atmosphere during this time. Tests of up to twelve weeks duration have been completed for distilled fractions of acetonitrile, dimethylformamide, N-nitrosodimethylamine, and propylene carbonate. In general, it can be said that distillation of these solvents did not produce a marked difference in physical characteristics. Refractive indices of the distilled solvent fractions did not differ significantly from the undistilled samples. One exception was N-nitrosodimethylamine. The refractive index of undistilled NDA at 25°C ranged from 1.4339 to 1.4340 over a four week period. The refractive index for the distilled fractions had an average value of 1.4344 to 1.4345 over the same period.

Fractional vacuum distillation decreased the specific conductivities of the above solvents in most cases. However, upon standing the electronic conductivities returned to values comparable to that of the undistilled sample. This can, perhaps, be attributed to the establishment of an equilibrium between the decomposition products of the solvent and the solvent itself. An example of this would be the formation of propylene glycol and carbon dioxide in propylene carbonate. Propylene carbonate was the only solvent whose specific conductivity was changed appreciably by distillation. The conductivity of undistilled propylene carbonate ranged from $1.37 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ to $1.45 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ over a twelve week period. The conductivity of distilled propylene carbonate ranged from $4.01 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ to $9.71 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ immediately after distillation. After twelve weeks these values had still not increased to that of the undistilled sample.

Results for the distillation and characterization of distilled acetonitrile, dimethylformamide, N-nitrosodimethylamine, and propylene carbonate are given in Table X, p. IV-83 through IV-87.

12. Electrochemical Half-Cell Screening of Anodes in Purified Solvents.

In addition to characterization of distilled solvents by means of electronic conductivity and refractive index measurements, distilled solvents were employed in half-cell screening tests. This was done to determine whether vacuum distillation of the solvents used in electrolytic solutions had a significant effect on electrochemical performance. During this period, lithium anodes were tested in three electrolytes in which the solvent had been vacuum distilled. These electrolytes were N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-dimethylformamide, morpholinium hexafluorophosphate-dimethylformamide, and N-phenyl-N,N,N-trimethylammonium hexafluorophosphate-N-nitrosodimethylamine. The electrochemical behavior of lithium in the first two electrolytes differed only slightly from its behavior in the same electrolytes made from undistilled dimethylformamide. Deterioration of the anode material seemed slightly greater in the distilled systems. Differences in anode voltage during the discharges were not significant and no conclusions could be made.

A lithium anode tested in an electrolyte of N-phenyl-N,N,N-trimethylammonium hexafluorophosphate in distilled N-nitrosodimethylamine exhibited a more marked difference from the undistilled system. The open circuit voltage of the lithium anode was -2.67 V compared to a value of -3.42 for the undistilled system. Voltages during the 0.1 and 1 ma/cm² discharges were also higher for the undistilled system. However, the lithium anode in the distilled electrolyte system maintained higher voltages during the 10 and 100 ma/cm² discharges. Less deterioration of the anode occurred when undistilled N-nitrosodimethylamine was employed. Gas evolution was evident in the distilled system and a precipitate was formed. This did not occur in the undistilled system.

Data for the electrochemical half-cell screening of anodes in purified electrolytes is given in Table XI, p. IV-88 through IV-92. The electrochemical data for similar half-cells, in which undistilled solvents were used, are also listed for comparison.

Four half-cell screening tests reported under electrochemical screening of anodes were conducted in distilled N-nitrosodimethylamine. The distilled solvent was used because a considerable amount of water had been detected in the solvent as received. The data for these half-cells is given in Table I, p. IV-1 through IV-14.

II. CURRENT PROBLEMS

II. CURRENT PROBLEMS

The major problem continues to be that of developing a cathode with suitable characteristics for a high energy density battery.

III. WORK TO BE PERFORMED

III. WORK TO BE PERFORMED

A. During the Next Quarter:

1. Anodes.

The anode half-cell screening program is essentially completed. Exceptions will be made for promising anode-electrolyte combinations. Future work will include linearly varying potential scans of anodes in electrolytes which permit higher discharge rates. Coulombic efficiency determinations will be made at 1, 10, and 50 ma/cm².

2. Cathodes.

Investigation of fabrication techniques will be continued in an effort to improve cathode conductivity. This will include fabrication of cathodes from non-stoichiometric compounds and attempts to form thin film electrodes. Electrochemical testing of organic cathode materials will be continued and efforts to identify the reduction products will be made. Linearly varying potential studies and coulombic efficiency determinations will continue to be made of promising cathodes.

3. Electrolytes.

Purification and characterization of solvents used in electrolytic solutions will be continued. Further studies will be made of electrolytes which permit higher anode discharge rates. These studies will include measurement of specific conductance, density, and viscosity at 25°C over a wide range of concentrations.

4. Components.

Further testing of separators, particularly when liquid or dissolved cathodes are employed, will be made. Separator materials being investigated include various ion exchange membranes, porous plastics, and filter paper. An investigation of case and lead materials for compatibility with electrolytes will be initiated.

5. Batteries.

Systems showing promise in half-cell screening tests will be assembled to yield information on problems associated with construction of complete systems.

B. During the Next Month:

1. Anodes.

Linearly varying potential studies will be made of promising anode-electrolyte combinations.

2. Cathodes.

Attempts will be made to fabricate thin film cupric fluoride cathodes by sintering on copper and aluminum foil. Linearly varying potential studies will be made of dissolved organic cathode materials. Coulombic efficiency studies will be continued.

3. Electrolytes.

Distillation of solvents used in electrolytic solutions will be continued. Characterization of these solvents will be extended to include analyses for water using the Karl Fischer method.

4. Components.

Full cell testing of several separating materials will be made. Two week stability for several case materials in various electrolytes will be performed.

IV. TEST RESULTS

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES

Page

I. Anode-Electrolyte Systems Capable of Sustaining 100 ma/cm².

A. Lithium Anode Systems. IV-3

<u>Solvent</u>	<u>Solute</u>
1. N-Nitrosodimethylamine (NDA)	LiPF ₆

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm².

A. Calcium Anode Systems. IV-4

1. Acetonitrile (AN)	LiPF ₆
2. Dimethylformamide (DMF)	NH ₄ PF ₆
3. NDA (Distilled)	LiPF ₆

B. Lithium Anode Systems. IV-6

*1. DMF	Tri-n-propylammonium hexafluoro-arsenate - (C ₃ H ₇) ₃ NHAsF ₆
2. NDA	LiPF ₆ , Morpholine - $\text{O} \begin{array}{c} \diagup \text{CH}_2\text{CH}_2 \diagdown \\ \text{CH}_2\text{CH}_2 \end{array} \text{NH}$

C. Magnesium Anode Systems. IV-8

1. AN	LiPF ₆
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III. Anode-Electrolyte Systems Capable of Sustaining 1 ma/cm².

A. Calcium Anode Systems. IV-9

1. AN	Tri-n-propylammonium hexafluoro-arsenate
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B. Magnesium Anode Systems. IV-10

1. NDA (Distilled)	LiPF ₆
2. NDA (Distilled)	Tetra-n-propylammonium hexafluoro-arsenate - (n-C ₃ H ₇) ₄ NAsF ₆

IV. Anode-Electrolyte Systems Capable of Sustaining 0.1 ma/cm².

A. Calcium Anode Systems. IV-11

1. DMF	Tetra-n-propylammonium hexafluoro-antimonate - (n-C ₃ H ₇) ₄ NSbF ₆
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* Electrolyte pretreated with lithium.

Each system is classified under the current density at which the anode exhibited less than 50% polarization from the initial open circuit potential.

All electrolytes are 1 molal in concentration.

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

Page

IV. Anode-Electrolyte Systems Capable of Sustaining 0.1 ma/cm^2 . (Continued)

B. Magnesium Anode Systems.

IV-12

Solvent

Solute

1. DMF

NH_4PF_6

V. Anode-Electrolyte Systems Which Cannot Sustain 0.1 ma/cm^2 .

A. Calcium Anode Systems.

IV-13

1. NDA (Distilled)

Tetra-n-propylammonium hexafluoro-arsenate

B. Magnesium Anode Systems.

IV-14

1. DMF

Tetra-n-propylammonium hexafluoro-antimonate

Each system is classified under the current density at which the anode exhibited less than 50% polarization from the initial open circuit potential. All electrolytes are 1 molal in concentration.

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES

I. Anode-Electrolyte Systems Capable of Sustaining 100 ma/cm².
A. Lithium Anode Systems.

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities		Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute				Current Density (ma/cm ²)		Initial	Final	
NDA	LiPF ₆ *	Ag/AgCl	Ag/AgCl	-3.33					Continuous gassing of the lithium anode. Slight gassing occurred at the counter electrode during the 100 ma/cm ² discharge. At the end of the discharges the lithium was covered with a gray film.
						-3.37	-3.32	-3.37	
						-3.36	-3.36	-3.37	
						-2.85	-3.20	-2.76	
					100	-2.83	-1.98	-1.84	

* 1 molal LiPF₆-NDA has a specific conductance of $1.92 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ (26°C).

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm².
A. Calcium Anode Systems.

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Various Current Densities	Voltage of Anode vs. Reference Electrode at Various Current Densities	Further Observations and Remarks
Solvent	Solute						Initial	Final	
1.	AN	LiPF ₆	Ag/AgCl	-2.66	-2.60 -2.61 -2.17 -2.27	0.1 1 10 100	-2.43 -1.83 -1.72 -1.28	-2.07 -2.01 -1.63 -1.10	The calcium anode became covered with a black film during the 10 ma/cm ² discharge. During the 100 ma/cm ² discharge vigorous gassing occurred at the calcium electrode and a black solid fell from its surface. The counter electrode also began gassing vigorously during the 100 ma/cm ² discharge. There was no change in the appearance of the reference electrode or the electrolyte.
2.	DMF	NH ₄ PF ₆	Ag/AgCl	-2.48	-2.50 -2.48 -2.34 -2.16	0.1 1 10 100	-2.48 -2.47 -2.35 -1.35	-2.50 -2.48 -2.25 Reversed Polarity	Continuous moderate gassing at the calcium anode. The solution became slightly turbid during discharge. The counter electrode began gassing during the 100 ma/cm ² discharge. The calcium anode was partially black at the end of the discharges. No change in the appearance of the reference electrode.

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm². (Continued)
A. Calcium Anode Systems. (Continued)

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute						Initial	Final	
NDA (Distilled)	LiPF ₆	Ag/AgCl	Ag/AgCl	-2.13	-2.27	0.1	-2.13	-2.22	The calcium gassed continuously and turned black. There were no other changes in the system.
					-2.26	1	-2.06	-2.06	
					-2.00	10	-1.83	-1.25	
					-1.87	100	Reversed	----	
							Polarity		

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm². (Continued)
B. Lithium Anode Systems.

Electrolyte		Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute	Reference Electrode	Counter Electrode		Initial	Final	
DMF	*	Ag/AgCl	Ag/AgCl		-3.10	-3.11 -2.94 -2.70 -0.97	The small liquid phase which had formed upon pretreatment with lithium became larger during discharge. A yellow-brown solid became suspended in solution at the counter electrode. At the end of the discharges the lithium was covered with a thin gray film.
				0.1	-3.00	-3.11	
				1	-2.82	-2.94	
				10	-2.63	-2.70	
				100	-0.84	-0.97	

9-IV

* (C₃H₇)₃NHAsF₆ - Tri-n-propylammonium hexafluoroarsenate (1 molal). The solution was pretreated with lithium metal until gas evolution ceased. Specific conductivity changed from 2.20 x 10⁻² (27°C) to 1.65 x 10⁻² (26°C) ohm⁻¹ cm⁻¹. The light orange solution became an opaque red-brown and a small, second liquid phase appeared. A solid formed which was removed from the solution by filtration.

The results for the same system not pretreated with lithium are listed below.

Electrolyte		Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute	Reference Electrode	Counter Electrode		Initial	Final	
DMF	**	Ag/AgCl	Ag/AgCl		-3.52	-3.52 -3.51 -3.28 -3.26	Vigorous gassing at the lithium electrode at all times. Rate of gassing decreased slightly as the test progressed. Discharges at each current density were limited to two minutes because of high apparent rate of self-discharge. (100 ma/cm ² system.)
				0.1	-3.52	-3.52	
				1	-3.50	-3.48	
				10	-3.08	-2.95	
				100	-2.28	-2.35	

** (C₃H₇)₃NHAsF₆ - Tri-n-propylammonium hexafluoroarsenate (1 molal)

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm². (Continued)
B. Lithium Anode Systems. (Continued)

Electrolyte	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
								Initial	Final	
2.	NDA	*	Ag/AgCl	Ag/AgCl	-2.93	-2.87	0.1	-2.92	-2.87	The lithium electrode gassed continuously. During the 100 ma/cm ² discharge gassing began at the counter electrode and deterioration was evident. There was no change in the appearance of the reference electrode or the electrolyte.
						-2.87	1	-2.85	-2.85	
						-2.87	10	-2.67	-2.68	
						-2.83	100	-1.40	-1.36	

The system whose reaction products might be LiPF₆ and morpholine is listed below for comparison.

NDA	**	Ag/AgCl	Ag/AgCl	-2.90	-2.91	0.1	-2.90	-2.91	Counter electrode gassed at 100 ma. No change in the appearance of the lithium, the reference electrode, or the electrolyte.
					-2.91	1	-2.87	-2.88	
					-2.90	10	-2.72	-2.68	
					-2.88	100	-1.60	-1.64	

* LiPF₆ (1 molal) and $O \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}$ - morpholine (1 molal). Specific conductance = 1.85×10^{-2} ohm⁻¹ cm⁻¹.

** $O \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}_2\text{PF}_6$ -morpholinium hexafluorophosphate (1 molal). The solution was pretreated with lithium metal until gas evolution ceased. This reaction resulted in the formation of a gelatinous yellow solid in addition to the evolution of an appreciable quantity of gas. After filtering the solution had a specific conductance of 1.81×10^{-2} ohm⁻¹ cm⁻¹ as compared to 2.74×10^{-2} ohm⁻¹ cm⁻¹ for the untreated solution.

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm². (Continued)
 C. Magnesium Anode Systems.

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute						Initial	Final	
AN	LiPF ₆	Ag/AgCl	Ag/AgCl	-1.36	-1.33	0.1	-1.23	-1.22	During the 100 ma/cm ² discharge the magnesium surface became covered with a thin gray film and gassing began at the counter electrode. There was no change in the appearance of the reference electrode or the electrolyte.
					-1.34	1	-1.12	-1.26	
					-1.27	10	-1.15	-1.21	
					-1.35	100	-0.75	-0.61	

1.

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

III. Anode-Electrolyte Systems Capable of Sustaining 1 ma/cm².

A. Calcium Anode Systems.

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode		Open Circuit Voltage After Discharge at Various Current Densities		Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute			Initial	Open Circuit Voltage of Anode vs. Reference Electrode	Initial	Open Circuit Voltage After Discharge at Various Current Densities		Initial	Final	
AN	*	Ag/AgCl	Ag/AgCl	-1.13		-0.97		0.1	-0.80	-0.92	The calcium surface became covered with a black film during the discharges. There was no change in the appearance of the counter electrode, the reference electrode, or the electrolyte.
						-1.75		1	-0.60	-0.84	
						-1.24		10	-0.37	-0.49	
						-1.75		100	Reversed Polarity	----	

* Tri-n-propylammonium hexafluoroarsenate - (n-C₃H₇)₃NHAsF₆

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

III. Anode-Electrolyte Systems Capable of Sustaining 1 ma/cm². (Continued)
 B. Magnesium Anode Systems.

Electrolyte	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
								Initial	Final	
1.	NDA (Distilled)	LiPF ₆	Ag/AgCl	Ag/AgCl	-1.10	-1.30	0.1	-1.25	-1.28	The magnesium anode began gassing during the 0.1 ma/cm ² discharge and reversed turned black during the 1 ma/cm ² Polarity discharge. There were no other changes in the system.
						-1.32	1	-1.24	-1.23	
						-1.16	10	-0.85	Reversed	
						----	100*	----	----	
2.	NDA (Distilled)	**	Ag/AgCl	Ag/AgCl	-1.07	-1.07	0.1	-0.99	-1.07	The magnesium anode became darker in color during the discharges. There were no other changes in the system.
						-1.07	1	-0.30	-1.00	
						-1.05	10	0.00	Reversed	
						----	100*	----	----	

* Not run.

** Tetra-n-propylammonium hexafluoroarsenate - (n-C₃H₇)₄NAsF₆

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

IV. Anode-Electrolyte Systems Capable of Sustaining 0.1 ma/cm².
A. Calcium Anode Systems.

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities		Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute				Initial	Open Circuit Voltage After Discharge at Various Current Densities		Initial	Final	
DMF	*	Ag/AgCl	Ag/AgCl	-1.97	-1.62	0.1	-1.81	-1.20	A thin gray film covered the calcium surface at the end of the discharges. There was no change in the appearance of the counter and reference electrodes or the electrolyte.	
					-2.04	1	-0.10	Reversed Polarity		
					----	10**	----	----		
					----	100**	----	----		

1.

* Tetra-n-propylammonium hexafluoroantimonate - (n-C₃H₇)₄NSbF₆
** Not run.

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

IV. Anode-Electrolyte Systems Capable of Sustaining 0.1 ma/cm². (Continued)
 B. Magnesium Anode Systems.

Electrolyte			Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities		Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute	Reference Electrode		Counter Electrode	Initial		Final	Initial	
DMF	NH ₄ PF ₆	Ag/AgCl	Ag/AgCl	-1.56	-1.53 -1.33 ---- ----	0.1 1 10* 100*	-1.25 Reversed Polarity ---- ----	-1.43 ---- ---- ----	No change in the appearance of the entire system.

* Not run.

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

V. Anode-Electrolyte Systems Which Cannot Sustain 0.1 ma/cm².
A. Calcium Anode Systems.

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute						Initial	Final	
1. NDA (Distilled)	*	Ag/AgCl	Ag/AgCl	-1.75	-1.47 -1.65 -1.86 ----	0.1 1 10 100**	-1.38 -0.20 -0.07 ----	-0.52 -0.20 -0.07 ----	The calcium began gassing during the 1 ma/cm ² discharge. The polarity of the anode reversed briefly at the beginning of the 1 and 10 ma/cm ² discharges but returned quickly to a negative value.

IV-13

* Tetra-n-propylammonium hexafluoroarsenate - (n-C₃H₇)₄NAsF₆
** Not run.

TABLE I. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

V. Anode-Electrolyte Systems Which Cannot Sustain 0.1 ma/cm². (Continued)
 B. Magnesium Anode Systems.

Electrolyte			Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute	Initial						Final		
DMF	*	Ag/AgCl	Ag/AgCl	-1.12	-1.16	0.1	-0.70	Reversed Polarity	Reversal at 0.1 ma occurred after less than a minute of discharge. No change in the appearance of the entire system.	
					----	1**	----	----		
					----	10**	----	----		
					----	100**	----	----		

* Tetra-n-propylammonium hexafluoroantimonate - (n-C₃H₇)₄NSbF₆

** Not run.

FIGURE 1a. LINEARLY VARYING POTENTIAL SCANS OF A LITHIUM ANODE IN 1 MOLAL N-PHENYL-N,N,N-TRIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYL-FORMAMIDE ELECTROLYTE. Ag/AgCl COUNTER AND REFERENCE ELECTRODES. ANODE AREA - APPROXIMATELY 10 mm^2 . OPEN CIRCUIT VOLTAGE = -3.20 V .

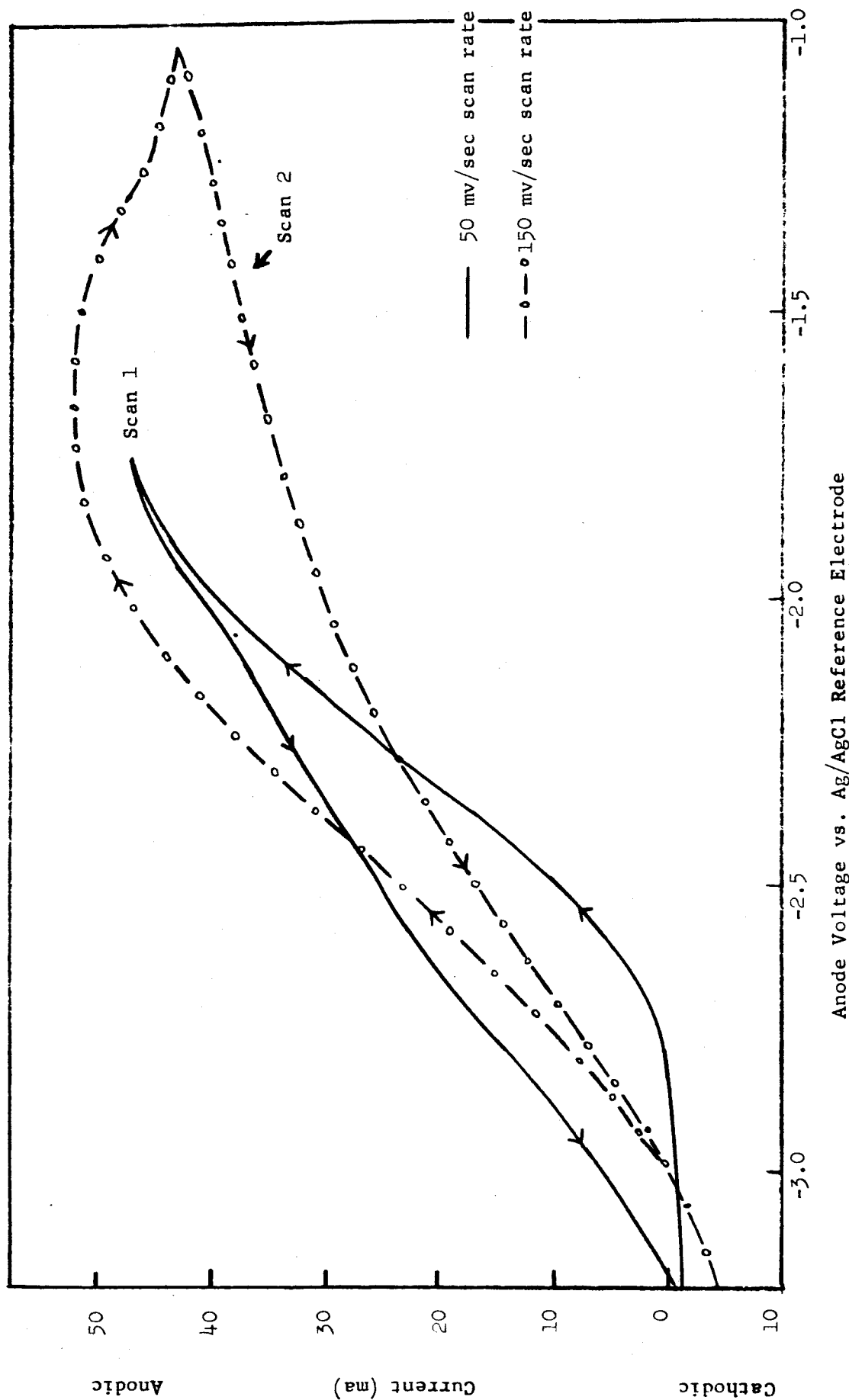


FIGURE 1b. LINEARLY VARYING POTENTIAL SCANS OF A LITHIUM ANODE IN 1 MOLAL N-PHENYL-N,N-TRIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYL-FORMAMIDE ELECTROLYTE. Ag/AgCl COUNTER AND REFERENCE ELECTRODES. ANODE AREA - APPROXIMATELY 10 mm^2 . OPEN CIRCUIT VOLTAGE = -3.20V . (Continued)

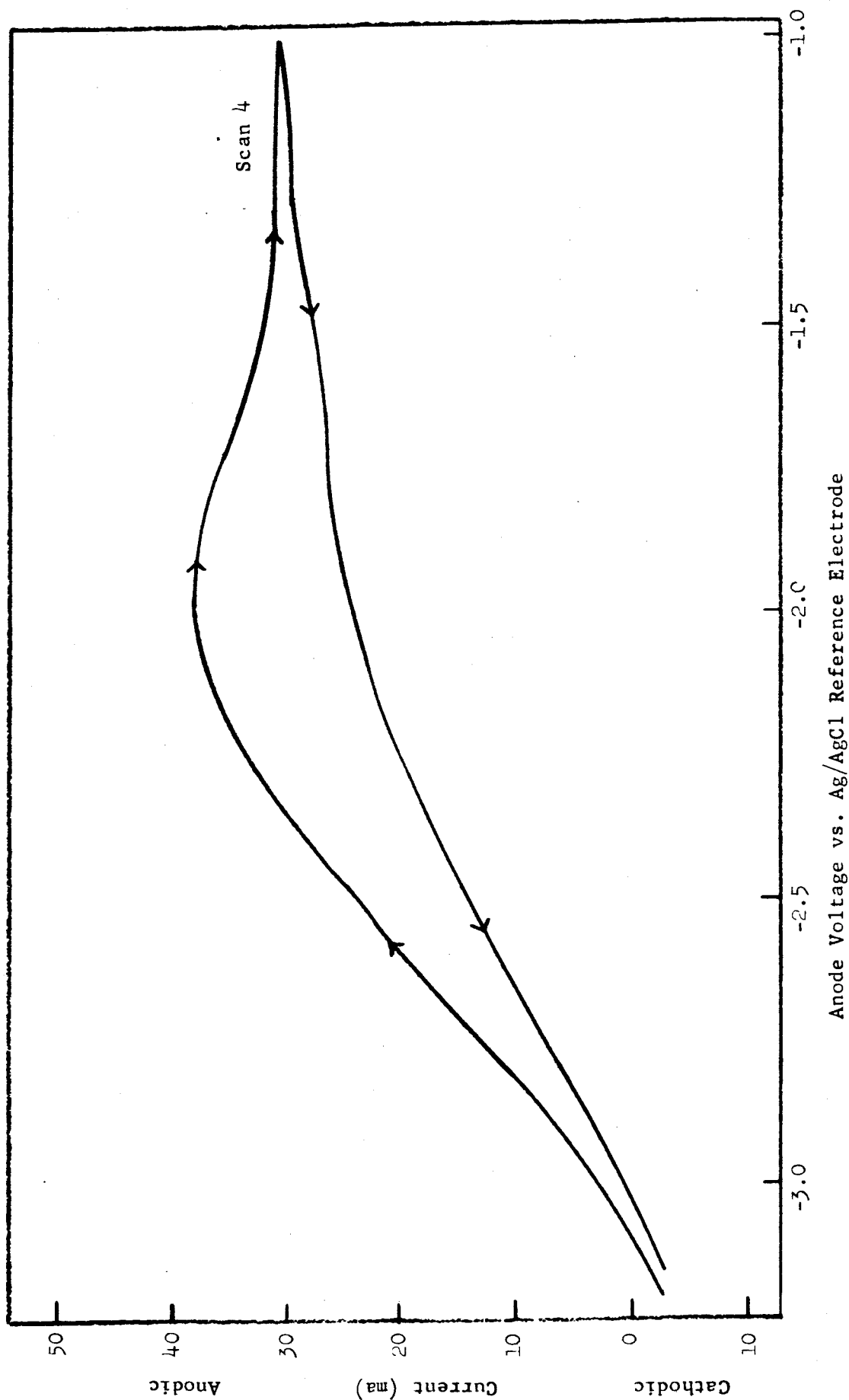


TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES

	<u>Page</u>
A. Cupric Chloride Cathode.....	IV-18
B. Cuprous Chloride Cathode.....	IV-19
C. Cuprous Chloride-Cupric Chloride Mixed Salt Cathode.....	IV-20
D. Cupric Fluoride Cathode.....	IV-21
E. Cupric Fluoride Cathodes from which Phenol was Sublimed to Increase Porosity.....	IV-22
F. Cupric Fluoride Filter Pad Cathode.....	IV-23
G. Cupric Fluoride-Cobalt Trifluoride Mixed Salt Cathodes.	
1. Cathode prepared from $\text{CuF}_2\text{-CoF}_3$ mixture heated at 300°C	IV-24
2. Cathode prepared from $\text{CuF}_2\text{-CoF}_3$ mixture recovered from pyridine.....	IV-25
H. Cupric Fluoride-Ferric Fluoride Mixed Salt Cathodes.	
1. Cathode prepared from $\text{CuF}_2\text{-FeF}_3$ mixture heated at 760°C	IV-26
2. Cathode prepared from $\text{CuF}_2\text{-FeF}_3$ mixture recovered from pyridine.....	IV-27
I. Cupric Fluoride-Lithium Fluoride Mixed Salt Cathodes.	
1. Cathode prepared from $\text{CuF}_2\text{-LiF}$ mixture heated at 350°C	IV-28
2. Cathode prepared from $\text{CuF}_2\text{-LiF}$ mixture recovered from pyridine.....	IV-29
J. Cupric Oxychloride Cathode.....	IV-30
K. Manganese Dioxide Cathode.....	IV-31
L. Silver Difluoride Cathodes.....	IV-32
M. Silver Fluoride Cathode.....	IV-33
N. Silver Oxide Cathodes.....	IV-34
O. Silver Fluoride-Silver Oxide Mixed Salt Cathode.	
1. Silver fluoride containing a small percentage of Ag_2O as shown by X-ray diffraction.....	IV-36
2. A mixture of 75 wt. % AgF and 25 wt. % AgF containing Ag_2O impurities.....	IV-37

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES

A. Cupric Chloride Cathode.

Experimental Details:

Cathode matrix - nickel screen.

Matrix size - 1 cm² (circular).Cathode preparation - the nickel screen was dipped into molten CuCl₂*.Electrolyte - 1 molal (C₆H₅)(CH₃)₃NPF₆** - dimethylformamide (DMF).

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)							Observations and Remarks
	0	0.1	1	5	10	50	100	
Initial	+0.20	+0.02	-0.20	-0.27	-0.33	-0.92	-1.60	Cathode became copper-colored during the discharges.
Final	-0.08	-0.10	-0.13 (3 min.)	-0.20 (3 min.)	-0.27 (3 min.)	-0.89 (3 min.)	-1.72 (2 min.)	

* X-ray diffraction indicated the possible presence of CuO.

** N-Phenyl-N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

B. Cuprous Chloride Cathode.

Experimental Details:

Cathode matrix - copper screen.

Matrix size - 1 cm^2 (circular).Cathode preparation - the copper screen was dipped into molten Cu_2Cl_2^* .Electrolyte - 1 molal $(\text{C}_6\text{H}_5)_3\text{NPF}_6^{**}\text{-DMF}$.Counter electrode - lithium. Reference electrode - Ag/AgCl .

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)							Observations and Remarks
	0	0.1	1	5	10	25	50	
Initial	+0.04	0.00	-0.28	-0.47	-0.55	-0.63	-2.00	Slow gas evolution began at the cathode during the 50 ma/cm ² discharge. The cathode became copper-colored during the discharge.
Final	+0.02	+0.005	-0.20	-0.30 (3 min.)	-0.40 (2 min.)	-0.61 (2 min.)	-1.28 (1 min.)	

* All X-ray diffraction peaks corresponded to those of Cu_2Cl_2 . X-ray fluorescence indicated the presence of Ni, Fe, Cr and Ca contaminants.

** N-Phenyl-N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

C. Cuprous Chloride-Cupric Chloride Mixed Salt Cathode.

Experimental Details:

Cathode matrix - nickel screen.
 Matrix size - 1 cm² (circular).
 Composition of cathode mix - 75 wt. % Cu₂Cl₂, 25 wt. % CuCl₂*.
 Cathode preparation - the nickel screen was dipped into the molten Cu₂Cl₂-CuCl₂ mixture.
 Electrolyte - 1 molar (C₆H₅)(CH₃)₃NPF₆**--DMF.
 Counter electrode - lithium. Reference electrode - Ag/AgCl.
 Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference Electrode at Various Current Densities							
Time of Measurement	(ma/cm ²)						
	0	0.1	1	5	10	50	100
Initial	+0.07	+0.06	-0.10	-0.17	-0.22	-0.96	-1.63
Final	-0.07	+0.03	-0.08	-0.14	-0.21 (4 min.)	-0.78 (3 min.)	-1.34
Observations and Remarks							Solution turned dark green. Slight gassing occurred. The cathode became copper-colored during the discharge.

* X-ray diffraction peaks of Cu₂Cl₂ were slightly displaced, possibly because of formation of a CuCl₂-Cu₂Cl₂ solid solution. X-ray fluorescence indicated the presence of Ni, Fe and Cr in addition to Cu.

** N-Phenyl-N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)D. Cupric Fluoride Cathode.

Experimental Details:

Cathode matrix - silver grid.
 Matrix size - 1 cm² (circular).
 Composition of cathode mix - 92 wt. % CuF₂, 5 wt. % Solka-Floc, 3 wt. % acetylene black (Shawinigan).
 Dry-press formation pressure - 10,000 lb./cm²
 Electrolyte - 1 molal (C₆H₅)(CH₃)₃NPF₆*-dimethylformamide.
 Counter electrode - lithium. Reference electrode - Ag/AgCl.
 Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)					Observations and Remarks
	0	0.1	1	5	10	
Initial	+0.33	+0.25	+0.15	-0.09	-0.60	The cathode material began to separate from the silver support grid during the 5 ma/cm ² discharge. There were no other changes in the system.
Final	-0.02	+0.21	+0.03	-0.44	-1.30 (3 min.)	

* N-phenyl N,N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

E. Cupric Fluoride Cathodes from which Phenol was Sublimed to Increase Porosity.

Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm² (circular).

Weight of cathodes before sublimation - (1) 0.5965 g; (2) 0.6134 g.

Composition of cathode mix - 62.5 wt. % CuF₂, 2.5 wt. % carbon black (14R-22 Columbian Carbon Co.), 5 wt. % Solka-Floc, 30 wt. % phenol.Dry-press formation pressure - 6,000 lb./cm².

Sublimation of phenol - sublimed at ca. 140°C in an argon atmosphere until constant weight was attained (ca. 3 hours).

Percentage of initial weight of phenol lost - (1) 114%; (2) 113%. Apparently a small amount of volatile substance in addition to phenol was lost.

Electrolyte - (C₆H₅)(CH₃)₃NPF₆*-DMF.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference
Electrode at Various Current Densities

Cathode Number	Time of Measurement	(ma/cm ²)				Observations and Remarks
		0	0.1	1	5	
1	Initial	+0.20	+0.20	+0.12	-0.60	In both cases the portion of the cathode facing the counter electrode fell off the expanded metal matrix during the 1 ma/cm ² discharge.
	Final	+0.02	+0.16	-0.18	-1.00 (48 sec.)	
2	Initial	+0.21	+0.20	+0.13	-0.65	
	Final	-0.03	+0.17	-0.20	-1.00 (38 sec.)	

* N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

F. Cupric Fluoride Filter Pad Cathode.

Experimental Details:

Cathode matrix - nickel expanded metal.

Matrix size - 1 cm² area.

Composition of cathode mix - 78 wt. % CuF₂, 11 wt. % filter paper pulp, 11 wt. %

Dixon graphite No. 200-43.

Dry-press formation pressure - 20,000 lb./cm².

Preparation of the cathode - a heptane slurry of the above mixture was filtered on a Buchner funnel. From the resulting porous mat, 2" x 0.5" sections were cut. Sections were pressed onto both sides of a nickel expanded metal matrix at 20,000 lb./cm².

Electrolyte* - 1 molar LiClO₄-propylene carbonate (PC).

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference
Electrode at Various Current Densities

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)					Observations and Remarks
	0	0.1	1	5	50	
Initial	+0.64	+0.63	+0.56	+0.20	-0.28	Clear, colorless solution turned green by the end of the discharge.
Final	+0.42	+0.61	+0.42	+0.043	-0.354	
					-2.2	---

* Specific conductivity = $5.98 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

G. Cupric Fluoride-Cobalt Trifluoride Mixed Salt Cathodes.

1. Cathode prepared from CuF_2 - CoF_3 mixture heated at 300°C .

Experimental Details:

Cathode matrix - Ag expanded metal (0.005" thickness).
Matrix size - 1 cm^2 (circular).

Weight of cathode (not including matrix) - 0.5 g.

Composition of mixed salt - 15.9 g. CuF_2 , 18.2 g. CoF_3 , (50 at. wt. % cobalt).

Preparation of mixed salt - the above mixture was heated in an argon atmosphere for 15 minutes at 300°C *. The resulting salt mixture retained the brown color of CoF_3 and the light gray color of CuF_2 but was covered with a rose-colored layer, possibly CoF_2 .

Composition of cathode mix - 95 wt. % salt mixture of CuF_2 and CoF_3 , 5 wt. % Solka-Floc. Dry-press formation pressure - 20,000 lb./ cm^2 .

Electrolyte - 1 molar $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ ** - DMF.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference

Electrode at Various Current Densities

Time of Measurement	Electrode at Various Current Densities (ma/ cm^2)			Observations and Remarks
	0	0.1	1	
Initial	+0.09	+0.05	-0.04	Slow, continuous gassing at the lithium electrode. Gassing began at the cathode during the 1 ma discharge.
Final	+0.04	+0.04	-1.22	

* Temperature reached 350°C for a brief period of time. During this time, white fumes appeared.

** N-Phenyl-N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

G. Cupric Fluoride-Cobalt Trifluoride Mixed Salt Cathodes. (Continued)

2. Cathode prepared from $\text{CuF}_2\text{-CoF}_3$ mixture recovered from pyridine.

Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm^2 (circular).

Weight of cathode (not including matrix) - 0.5 g.

Composition of $\text{CuF}_2\text{-CoF}_3$ salt mixture - 15.9 g. CuF_2 , 18.2 g. CoF_3 , (50 at. wt. % cobalt).

Preparation of mixed salt - 15.9 g. CuF_2 in 600 ml of pyridine and 18.2 g. CoF_3 in 300 ml of pyridine were combined. Both salts were only partially soluble in pyridine. The combined mixture was heated on a hot plate until all the liquid had evaporated. The resulting salt was dried at 110°C , pulverized and dried in a vacuum oven at 110°C and 29 mm Hg. The dried salt mixture was light brown. The mixture was combined with Solka-Floc and dry-pressed to form a pellet.

Composition of cathode mix - 95 wt. % $\text{CuF}_2\text{-CoF}_3$ salt mixture, 5 wt. % Solka-Floc.

Dry-press formation pressure - 20,000 lb./ cm^2 .

Electrolyte - 1 molal $(\text{C}_6\text{H}_5)_3(\text{CH}_3)_3\text{NPF}_6^*\text{-DMF}$.

Counter electrode - lithium. Reference electrode - Ag/AgCl .

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference
Electrode at Various Current Densities
(ma/cm^2)

Time of Measurement	0	0.1	1	5	Observations and Remarks
Initial	+0.135	+0.07	-0.07	-1.5	Continuous gassing of the lithium electrode. During discharge the yellow-green electrolyte became more yellow in the cathode area.
Final	-0.12	+0.022	-1.02	-2.3 (2 min.)	

* N-Phenyl-N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

H. Cupric Fluoride-Ferric Fluoride Mixed Salt Cathodes.

1. Cathode prepared from $\text{CuF}_2\text{-FeF}_3$ mixture heated at 760°C .

Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm^2 (circular).Weight of cathode - 0.7 g . (not including matrix).Composition of $\text{CuF}_2\text{-FeF}_3$ salt mixture - $90\text{ wt. } \%$ CuF_2 , $10\text{ wt. } \%$ FeF_3 .

Preparation of mixed salt - the above mixture was placed in a zircon combustion boat in a furnace at ca. 760°C until it melted. The mixture fumed before melting and in the molten state. The resulting substance was black with gray spots. X-ray diffraction patterns indicated approximately 50% CuO formation from CuF_2 . A shift in CuF_2 peaks was observed which might be attributed to formation of $\text{CuF}_2\text{-FeF}_3$ solid solution.

Composition of cathode mix - ca. $95\text{ wt. } \%$ salt mixture, ca. $5\text{ wt. } \%$ Solka-Floc.Dry-press formation pressure - $20,000\text{ lb./cm}^2$.Electrolyte - $1\text{ molal } (\text{C}_6\text{H}_5)_3\text{NPF}_6^*\text{-DMF}$.Counter electrode - lithium. Reference electrode - Ag/AgCl .Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference
Electrode at Various Current Densities

Time of Measurement	0	0.1	1	5	Observations and Remarks
Initial	+0.06	-0.05	-1.80	-2.10	The electrolyte changed from light yellow to deep yellow. Slow, continuous gassing of the lithium electrode. No change in the appearance of the cathode.
Final	+0.02	-0.38	-1.50	-2.10 (4 min.)	

* N-Phenyl-N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

H. Cupric Fluoride-Ferric Fluoride Mixed Salt Cathodes. (Continued)

2. Cathode prepared from $\text{CuF}_2\text{-FeF}_3$ mixture recovered from pyridine.

Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm^2 (circular).

Weight of cathode (not including matrix) - 0.5 g.

Composition of $\text{CuF}_2\text{-FeF}_3$ salt mixture - 17.3 g. CuF_2 , 1.34 g. FeF_3 , (7 at. wt. % Fe).

Preparation of mixed salt - 17.3 g. CuF_2 in 600 ml of pyridine and 1.34 g. FeF_3 in 200 ml of pyridine were combined. Both salts were only partially soluble in pyridine.

The combined solution was heated on a hot plate until all the liquid had evaporated.

The resulting salt was dried at 110°C , pulverized and dried in a vacuum oven at 110°C and 29 mm Hg. The dried salt was light blue-green. The dried salt mixture was combined with Solka-Floc and dry-pressed to form a cathode pellet.

Composition of cathode mix - 95 wt. % $\text{CuF}_2\text{-FeF}_3$ salt mixture, 5 wt. % Solka-Floc.

Dry-press formation pressure - 20,000 lb./ cm^2 .

Electrolyte - 1 molar $(\text{C}_5\text{H}_5)(\text{CH}_3)_3\text{NPF}_6\text{-DMF}$.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/ cm^2)			Observations and Remarks
	0	0.1	1	
Initial	-0.02	-0.315	-1.00	None.
Final	-0.50	-0.52	-1.65 (1 min.)	

* N-Phenyl-N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

I. Cupric Fluoride-Lithium Fluoride Mixed Salt Cathodes.

1. Cathode prepared from CuF_2 -LiF mixture heated at 850°C .

Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm^2 (circular).

Weight of cathode - 0.7 g. (not including matrix).

Composition of mixed salt - 0.92 g. LiF, 47.7 g. CuF_2 , (7 at. wt. % lithium).

Preparation of mixed salt - the above mixture was placed in a nickel combustion boat with a strip of nickel expanded metal and support grid were attacked. X-ray diffraction patterns of the resulting substance showed strong peaks for Cu_2O , Cu, and an unidentified substance, possibly a CuF_2 -LiF compound not listed in the ASTM Powder Index. A small amount of Li_2O was also indicated. No nickel was present. Because the attempt to fuse the mixture on an expanded nickel support grid failed, the mixture was used to make a dry-pressed cathode on silver expanded metal.

Composition of cathode mix - 95 wt. % CuF_2 -LiF salt product, 5 wt. % Solka-Floc.

Dry-press formation pressure - 20,000 lb./ cm^2 .

Electrolyte - 1 molal $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6^*\text{-DMF}$.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/ cm^2)				Observations and Remarks
	0	0.1	1	5	
Initial	+0.04	+0.01	-0.50	-1.80	Slow gassing at the lithium anode during the entire discharge. Gassing began at the cathode during the 5 ma discharge.
Final	-0.50	-0.06	-1.04	-2.10 (4 min.)	

* N-Phenyl-N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

- I. Cupric Fluoride-Lithium Fluoride Mixed Salt Cathodes. (Continued)
2. Cathode prepared from CuF_2 -LiF mixture recovered from pyridine.

Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm^2 (circular).

Weight of cathode (not including matrix) - 0.5 g.

Composition of CuF_2 -LiF salt mixture - 47.7 g. CuF_2 , 0.92 g. LiF, (7 at. wt. % Li).

Preparation of mixed salt - 0.92 g. LiF in 100 ml pyridine and 47.7 g. CuF_2 in 900 ml pyridine were stirred for approximately 5 hours until the limit of solubility had been reached. LiF was apparently completely insoluble in pyridine while CuF_2 was partially soluble and formed a blue solution. The two solutions and any solid present were mixed and stirred for approximately 3 hours. The resulting solution was heated on a hot plate until all the liquid had evaporated. The salt remaining was dried at 110°C , pulverized and vacuum dried at 110°C and 29 mm Hg. The dried salt mixture was gray-green (CuF_2 is light gray; LiF is white). The dried salt mixture was combined with Solka-Floc and dry-pressed to form a cathode pellet.

Composition of cathode mix - 95 wt. % CuF_2 -LiF salt mixture, 5 wt. % Solka-Floc.

Dry-press formation pressure - 20,000 lb./ cm^2 .

Electrolyte - 1 molal $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6^*$ -DMF.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference Electrode at Various Current Densities					Observations and Remarks
Time of Measurement	(ma/cm ²)				
	0	0.1	1	5	
Initial	+0.08	+0.02	-0.09	-2.0	Pale yellow electrolyte turned dark green. Continuous gassing at the lithium electrode.
Final	-0.10	-0.02	-0.80	-2.19 (3 min.)	

* N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

J. Cupric Oxychloride Cathode.

Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm² (circular).

Cathode preparation - 4 g. of CuCl₂·2H₂O and 6 g. CuO were mixed and heated at ca. 100°C for approximately two hours. Enough water was added to the mixture to form a slurry.

The slurry was heated at 100°C to remove some of the water. The resulting substance was pasted on the silver matrix and dried at 100°C for 1-1/2 hours. The dried paste

electrode was light green and was insoluble in water. The electrode was presumed to be cupric oxychloride, CuCl₂·3CuO·4H₂O.

Electrolyte - 1 molar (C₆H₅)(CH₃)₃NPF₆*-dimethylformamide.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference
Electrode at Various Current Densities

Time of Measurement	0	0.1	1	5	Observations and Remarks
Initial	+0.13	+0.09	-0.08	-0.20	The cathode maintained its mechanical integrity although it may have partially dissolved in the electrolyte. There were no apparent changes in the system.
Final	-0.05	+0.07	-0.07	-1.78	

* N-phenyl N,N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

K. Manganese Dioxide Cathode.

Experimental Details:

Cathode matrix - silver expanded metal
 Matrix size - 1 cm² (circular).
 Weight of cathode - 0.4919 g. (not including matrix).
 Composition of cathode mix - 64.5 wt. % MnO₂, 32.1 wt. % phenol, 3.4 wt. % Solka-Floc.
 Dry-press formation pressure - 4,000 lb./cm².
 Sublimation of phenol - sublimed at ca. 45°C and ca. 1-7 mm pressure until constant weight was attained (ca. 19 hours). % phenol sublimed - not determined.
 Electrolyte - 1 molar (C₆H₅)(CH₃)₃NPF₆*-DMF.
 Counter electrode - lithium. Reference electrode - Ag/AgCl.
 Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)		Observations and Remarks
	0	0.1	
Initial	-0.01	-0.05	None.
Final	-0.05	-0.90	

* N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)L. Silver Difluoride*Cathodes.

Experimental Details:

Cathode matrix - silver expanded metal.
 Cathode size - 1 cm^2 (circular). 2 mm thick.
 Composition of cathode mix - 95 wt. % AgF_2 , 5 wt. % Solka-Floc.
 Dry-press formation pressure - 15,000 lb./ cm^2 .
 Electrolyte - 1 molal AlCl_3 -acetonitrile (AN).
 Counter electrode - magnesium. Reference electrode - Ag/AgCl .
 Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Cathode Number	Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/ cm^2)						Observations and Remarks
		0	0.1	1	5	10	25	
1.	Initial	**	+0.08 (1-1/2 min.)	+0.10	-0.04	-0.12	-0.50	-0.72
	Final	+0.05	+0.11 (3 min.)	+0.14	+0.07	-0.07	-0.42	-1.50 (2-1/2 min.)
2.	Initial	+0.22	+0.22	+0.21	+0.02	-0.15	-0.62	-0.90
	Final	-0.02	+0.25	+0.23	+0.06	-0.13	-0.56	-3.5 (2-1/2 min.)

* Analysis by means of electrodeposition confirmed that the sample was AgF_2 .

** Reading was invalid because contact between the electrolyte and the leads caused a short in the system.

TABLE VI. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

M. Silver Fluoride* Cathode.

Experimental Details:

Cathode matrix - silver expanded metal.
 Matrix size - 1 cm^2 (circular).
 Cathode preparation - Ag expanded metal matrix was dipped in molten AgF.
 Electrolyte** - MgCl_2 -N-nitrosodimethylamine.
 Counter electrode - lithium. Reference electrode - Ag/AgCl.
 Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)			Observations and Remarks
	0	0.1	1	
Initial	+0.053	+0.025	-1.15	Cathode surface became slightly white.
Final	+0.142	+0.012	-1.26 (2 min.)	

* 100% AgF as shown by X-ray diffraction.

** Specific conductivity = $5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

N. Silver Oxide Cathodes.

1. Experimental Details:

Cathode matrix - silver metal. Cathode mix - 100% AgO.
 Dry-press formation pressure - 10,000 lb./cm².
 Electrolyte - 1 molar KAsF₆-dimethylformamide (DMF).
 Counter electrode - lithium. Reference electrode - Ag/AgCl.
 Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)					Observations and Remarks
	0	0.1	1	5	10	
Initial	+0.28	+0.25	-0.05	-0.45	-0.70	The AgO pellet was very brittle. Slight gassing occurred when the AgO was immersed in solution. At the end of the discharges the cathode was gray with a black center.
Final	-0.36	+0.18	-0.16	-0.64	-1.07 (1.5 min.)	

2. Experimental Details:

Cathode matrix - silver metal. Cathode mix - 100% AgO.
 Dry-press formation pressure - 15,000 lb./cm².
 Electrolyte - 1 molar (C₆H₅)(CH₃)₃NPF₆*-DMF.
 Counter electrode - lithium. Reference electrode - Ag/AgCl.
 Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)					Observations and Remarks
	0	0.1	1	5	10	
Initial	+0.58	+0.57	+0.48	-0.08	-0.52	The AgO pellet was very brittle. Slight gassing occurred when the AgO was immersed in solution. At the end of the discharges the AgO surface was still black but was partially covered with a loosely-adherent white solid.
Final	+0.04	+0.55	+0.12	-0.30	-0.69	
				-0.75	-0.92	

* N-Phenyl N,N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)N. Silver Oxide Cathodes. (Continued)

3. Experimental Details:

Cathode matrix - silver metal.

Weight of cathode (not including matrix) - 1 g.

Composition of cathode mix - 95 wt. % AgO, 5 wt. % Solka-Floc.

Dry-press formation pressure - 20,000 lb./cm².Electrolyte - 1 molar (C₆H₅)(CH₃)₃NPF₆*-DMF.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference
Electrode at Various Current Densities

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)				
	0	0.1	1	10	25
Initial	+0.60	+0.59	+0.50	-0.60	-0.48
Final	0.00	+0.58	+0.29	-0.52	-0.88
				(1 min.)	

Observations and Remarks

Gassing began when the cathode was inserted in the electrolyte. During the 10 ma/cm² discharge a white solid appeared on the AgO surface. At the end of the discharges a large amount of white solid had formed.

Most of the solid dissolved when the solution was stirred. The green electrolyte had turned clear yellow. The cathode remained unchanged.

The cell was allowed to discharge spontaneously at 50, 60 and 80 ma/cm² giving cathode voltages of -1.10, -1.42 and -1.78 respectively.

After the discharges the cathode was analyzed by X-ray diffraction and fluorescence. These methods indicated that the cathode surface was 100% silver metal.

* N-Phenyl N,N-trimethylammonium hexafluorophosphate

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

O. Silver Fluoride-Silver Oxide Mixed Salt Cathodes.*

1. Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm^2 (circular).

Cathode preparation - Ag expanded metal support grid was dipped in molten AgF until a sufficient amount solidified on the screen.

Electrolyte - MgCl_2 -N-nitrosodimethylamine.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Time of Measurement	Voltage of Cathode vs. Reference Electrode at Various Current Densities (ma/cm ²)				Observations and Remarks
	0	0.1	1	5	
Initial	+0.142	+0.025	-0.40	-1.40	Cathode surface became slightly white.
Final	+0.043	-0.005	-0.460	----	

* AgF containing a small amount of Ag_2O as shown by X-ray diffraction.

TABLE II. ELECTROCHEMICAL HALF-CELL SCREENING OF CATHODES (Continued)

O. Silver Fluoride-Silver Oxide Mixed Salt Cathodes.* (Continued)

2. Experimental Details:

Cathode matrix - silver expanded metal.

Matrix size - 1 cm² (circular).

Cathode preparation - Ag expanded metal support grid was dipped in molten AgF mixture until a sufficient amount for test purposes was deposited on the screen.

Electrolyte - MgCl₂-N-nitrosodimethylamine.

Counter electrode - lithium. Reference electrode - Ag/AgCl.

Duration of discharge at each current density - 5 minutes (unless noted otherwise).

Voltage of Cathode vs. Reference
Electrode at Various Current Densities

Cathode Number	Time of Measurement	Electrode at Various Current Densities (ma/cm ²)				Observations and Remarks
		0	0.1	1		
1	Initial	+0.205	+0.11	-0.090		None.
	Final	+0.047	+0.192	-0.50		

Experimental Details:

Cathodes 2 and 3 were run in a 1 molal (C₆H₅)(CH₃)₃NPF₆**DMF electrolyte. All other experimental conditions were the same as for cathode 1.

Cathode Number	Time of Measurement	Electrode at Various Current Densities (ma/cm ²)				Observations and Remarks
		0	0.1	1	10	
2	Initial	+0.65	+0.50	+0.40	-1.65	Cathode reacted upon insertion to form a white precipitate which increased during the 10 ma discharge.
	Final	+0.59	+0.46 (2 min.)	+0.26	----	
3	Initial	+0.60	+0.56	+0.45	+0.13	Cathode reacted with the electrolyte. A heavy white film formed on the cathode during the 5 ma discharge.
	Final	+0.52	+0.57	+0.46	+0.14	

* 75 wt. % AgF, 25 wt. % AgF containing Ag₂O impurities. (See footnotes on pages IV-33 and IV-36.)

** N-Phenyl N,N-trimethylammonium hexafluorophosphate

TABLE III. DISCHARGE OF CELLS UTILIZING
DISSOLVED ACTIVE CATHODE MATERIALS

	<u>Page</u>
A. Lithium/Platinized Carbon, Arsenic Trifluoride.....	IV-39
B. Lithium/Unplatinized Carbon, Arsenic Trifluoride.....	IV-41
C. Lithium/Unplatinized Carbon.....	IV-43

TABLE III. DISCHARGE OF CELLS UTILIZING
DISSOLVED ACTIVE CATHODE MATERIALS

A. Lithium/Platinized Carbon, Arsenic Trifluoride.

Anode - lithium. Area - 1 cm².

Cathode - a 1 cm x 1 cm x 3.8 cm rectangular piece of porous
speer HP-20 carbon with a 0.2 cm² hole bored 3.5 cm into one
end was platinized. 1.0 ml AsF₃ was placed in the holder.

Electrolyte - 1 molal (C₆H₅)(CH₃)₃NPF₆*-DMF.

Reference electrode - Ag/AgCl.

<u>Time (Minutes)</u>	<u>Cell Voltage</u>	<u>Cathode Voltage (vs. Ag/AgCl Reference Electrode)</u>	<u>Current (ma)</u>
0	3.39	+0.40	0
3	2.39	+0.16	20
9	1.90	-0.67	20
15	1.90	-0.72	15
17	1.80	-0.695	10
30	2.08	-0.73	10
60	2.08	-0.765	10
90	2.07	-0.78	10
120	2.04	-0.78	10
180	1.96	-0.78	10
240	1.94	-0.80	10
300	1.92	-0.80	10
360	1.92	-0.80	10
420	1.92	-0.80	10
480	1.92	-0.80	10
540	1.87	-0.80	10
600	1.84	-0.80	10
660	1.82	-0.80	10
720	1.80	-0.80	10
780	1.76	-0.80	10
840	1.72	-0.80	10
900	1.70	-0.80	10
960	1.68	-0.80	10

* N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate

TABLE III. DISCHARGE OF CELLS UTILIZING
DISSOLVED ACTIVE CATHODE MATERIALS (Continued)

A. Lithium/Platinized Carbon, Arsenic Trifluoride. (Continued)

<u>Time</u> <u>(Minutes)</u>	<u>Cell Voltage</u>	<u>Cathode Voltage</u> <u>(vs. Ag/AgCl</u> <u>Reference Electrode)</u>	<u>Current (ma)</u>
1020	1.70	-0.80	10
1050	1.68	-0.84	10
1080	1.72	-0.83	10
1140	1.95	-0.82	10*
1200	1.84	-0.84	10
1248	1.82	-0.82	10**
1260	1.96	-0.80	10
1320	1.84	-0.815	10
1380	1.82	-0.82	10
1440	1.84	-0.83	10
1470	1.84	-0.84	10
1500	1.88	-0.84	10
1560	1.88	-0.86	10
1620	1.88	-0.88	10
1680	1.86	-0.90	10
1740	1.84	-0.92	10
1800	1.80	-0.935	10
1860	1.80	-0.94	10
1920	1.72	-0.96	10
1980	1.55	-0.98	10
2040	1.36	-1.00	10

* Lithium electrode replaced.

** Fresh electrolyte added.

TABLE III. DISCHARGE OF CELLS UTILIZING
DISSOLVED ACTIVE CATHODE MATERIALS (Continued)

B. Lithium/Unplatinized Carbon, Arsenic Trifluoride.

Anode - lithium. Area - 1 cm².

Cathode - 1 cm x 1 cm x 3.8 cm rectangular piece of unplatinized porous Speer HP-20 carbon with a 0.2 cm² hole bored 3.5 cm into one end. 1 ml AsF₃ was placed in the holder.

Electrolyte - 1 molal (C₆H₅)(CH₃)₃NPF₆*-DMF.

Reference Electrode - Ag/AgCl.

<u>Time (Minutes)</u>	<u>Cell Voltage</u>	<u>Cathode Voltage (vs. Ag/AgCl Reference Electrode)</u>	<u>Current (ma)</u>
0	3.73	+0.05	0
0	----	-0.50	10
6	----	-0.63	10
10	2.20	-0.67	10
20	2.12	-0.70	10
24	----	-0.73	10
30	2.12	-0.73	10
36	----	-0.74	10
40	2.08	-0.74	10
50	2.06	-0.75	10
54	----	-0.76	10
60	2.04	-0.77	10
90	2.04	-0.78	10
120	2.04	-0.78	10
150	2.02	-0.79	10
180	2.00	-0.79	10
210	1.96	-0.80	10
240	1.93	-0.81	10
270	1.92	-0.82	10
300	1.92	-0.82	10
330	1.92	-0.82	10
368	1.92	-0.82	10
390	1.88	-0.82	10

* N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate

TABLE III. DISCHARGE OF CELLS UTILIZING
DISSOLVED ACTIVE CATHODE MATERIALS (Continued)

B. Lithium/Unplatinized Carbon, Arsenic Trifluoride. (Continued)

<u>Time (Minutes)</u>	<u>Cell Voltage</u>	<u>Cathode Voltage (vs. Ag/AgCl Reference Electrode)</u>	<u>Current (ma)</u>
420	1.92	-0.81	10
450	1.90	-0.81	10
480	1.89	-0.82	10
510	1.88	-0.82	10
540	1.88	-0.82	10
570	1.88	----	10
600	1.87	-0.82	10
660	1.86	-0.83	10
720	1.84	-0.83	10
780	1.84	-0.83	10
840	1.82	-0.84	10
900	1.88	----	10
960	1.92	----	10
1020	1.88	----	10
1080	1.83	----	10
1140	1.76	----	10
1200	1.64	----	10
1260	1.64	-0.80	10
1320	1.59	----	10
1360	1.39	----	10
1365	1.38	----	10
1367	0.60	----	10
1410	0.40	----	10

TABLE III. DISCHARGE OF CELLS UTILIZING
DISSOLVED ACTIVE CATHODE MATERIALS (Continued)

C. Lithium/Unplatinized Carbon*.

Anode - lithium. Area - 1 cm².

Cathode - 1 cm x 1 cm x 3.8 cm rectangular piece of porous Speer
 HP-20 carbon with a 0.2 cm² hole bored 3.5 cm into one end.

Electrolyte - 1 molal (C₆H₅)(CH₃)₃NPF₆** - DMF.

Reference electrode - Ag/AgCl.

<u>Time</u> <u>(Minutes)</u>	<u>Cell Voltage</u>	<u>Cathode Voltage</u> <u>(vs. Ag/AgCl</u> <u>Reference Electrode)</u>	<u>Current (ma)</u>
0	3	----	10
10	1.6	Reversed to -1.32 V.	10
20	1.53	----	10

* A porous carbon container identical to the ones used in the AsF₃ discharges was run in order to determine whether the carbon was electrochemically active in these systems.

** N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate

TABLE IV. COULOMBIC EFFICIENCIES OF CATHODES

	<u>Page</u>
Physical Details.....	IV-45
A. Cupric Fluoride Filter Pad Cathodes.	
B. Cupric Fluoride Filter Pad Cathodes Containing LiClO_4 .	
C. Lead Dioxide Cathodes.	
D. Silver Difluoride Cathodes.	
E. Silver Oxide Cathode.	
Electrochemical Details.....	IV-46
A. Cupric Fluoride Filter Pad Cathodes.	
B. Cupric Fluoride Filter Pad Cathodes Containing LiClO_4 .	
C. Lead Dioxide Cathodes.	
D. Silver Difluoride Cathodes.	
E. Silver Oxide Cathode.	

TABLE IV. COULOMBIC EFFICIENCIES OF CATHODES

Physical Details.

<u>Electrolyte</u>				<u>Weight of Electrolyte</u>
<u>Anode</u>	<u>(1 molal)</u>	<u>Volume of Electrolyte</u>		
A. Cupric Fluoride Filter Pad Cathodes (78 wt. % CuF ₂ , 11 wt. % Dixon graphite (No. 200-43), 11 wt. % filter paper pulp).				
1.	Li	LiClO ₄ -PC	30 ml	39.8 g
2.	Li	LiClO ₄ -PC	30 ml	39.5 g
3.	Li	LiClO ₄ -PC	30 ml	39.7 g
4.	Li	(C ₆ H ₅)(CH ₃) ₃ NPF ₆ *-DMF	30 ml	**
5.	Li	(C ₆ H ₅)(CH ₃) ₃ NPF ₆ *-DMF	23 ml	21.4 g
6.	Li	(C ₆ H ₅)(CH ₃) ₃ NPF ₆ *-DMF	30 ml	**
7.	Mg	AlCl ₃ -AN	30 ml	24.5 g
8.	Mg	AlCl ₃ -AN	30 ml	25.1 g
9.	Mg	AlCl ₃ -AN	30 ml	24.5 g
B. Cupric Fluoride Filter Pad Cathodes Containing LiClO ₄ (70.2 wt. % CuF ₂ , 10.0 wt. % LiClO ₄ , 9.9 wt. % Dixon graphite (No. 200-43), 9.9 wt. % filter paper pulp).				
1.	Li	LiClO ₄ -PC	30 ml	**
C. Lead Dioxide Cathodes (95 wt. % PbO ₂ , 5 wt. % Solka-Floc).				
1.	Li	MgCl ₂ -NDA	30 ml	**

* N-phenyl N,N,N-trimethylammonium hexafluorophosphate

** Not recorded

TABLE IV. COULOMBIC EFFICIENCIES OF CATHODES (Continued)

Physical Details. (Continued)				Weight of Electrolyte		
Anode	Electrolyte (1 molal)	Volume of Electrolyte				
D. Silver Difluoride Cathodes (95 wt. % AgF ₂ , 5 wt. % Solka-Floc).						
1. Mg	AlCl ₃ -AN	30 ml		*		
2. Mg	AlCl ₃ -AN	30 ml		*		
E. Silver Oxide Cathode (95 wt. % Ag ₂ O, 5 wt. % Solka-Floc).						
1. Li	(C ₆ H ₅)(CH ₃) ₃ NPF ₆ **--DMF	30 ml		*		
Electrochemical Details.						
Amount of Active Cathode Material	Milli-Equivalents	Discharge Current	Duration of Test	Coulombs Theoret. Actual	Coulombic Efficiency	Major Components Of Cathode After Discharge As Shown By X-Ray Diffraction
Cupric Fluoride Filter Pad Cathodes.						
0.173 g	3.41	1.5 ± 0.3 ma	1830 min.	329.1	164.7	50.0% Cu, graphite
0.268 g	5.28	5 ma	390 min.	508.7	117.0	23.0% CuF ₂ ·2H ₂ O, graphite
0.196 g	3.86	10.6 ± 0.6 ma	70 min.	372.5	44.5	11.9% Cu, graphite
0.234 g	4.61	1.46 ± 0.7 ma	7012 min.	444.9	614.3	138.1%*** Cu ₂ O
0.307 g	6.05	5 ma	1175 min.	583.1	352.8	60.5%***** CuF ₂ ·2H ₂ O, graphite
0.214 g	4.22	8.6 ± 1.3 ma	1574 min.	407.2	812.2	199.4%***** X-ray data not yet available

* Not recorded

** N-phenyl N,N-trimethylammonium hexafluorophosphate

*** Apparently material other than CuF₂ is contributing to the number of coulombs obtained

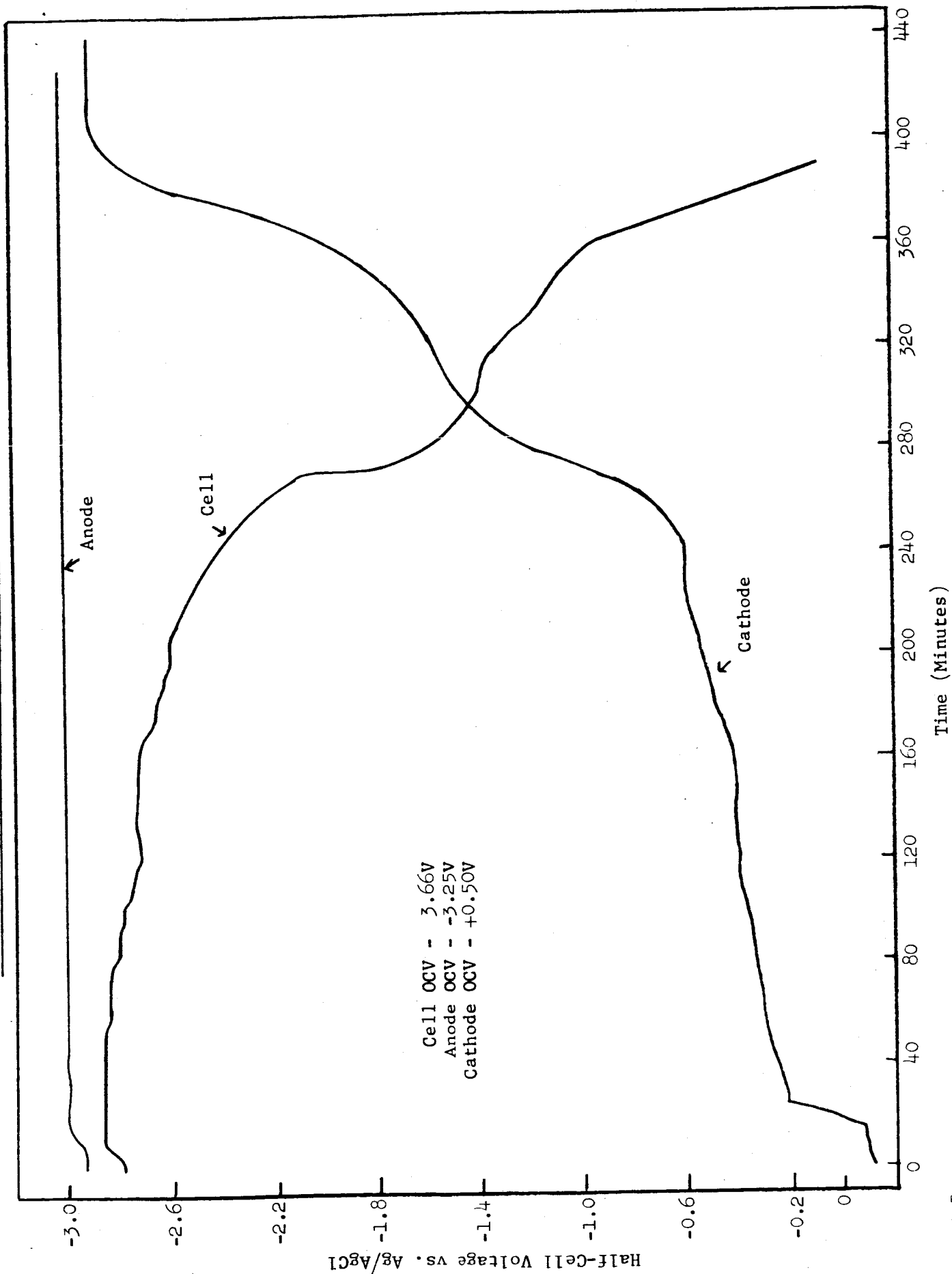
**** Test terminated before cut-off voltage of 0.2V for the cell was reached

TABLE IV. COULOMBIC EFFICIENCIES OF CATHODES (Continued)

Electrochemical Details. (Continued)					Major Components Of Cathode After Discharge As Shown By X-Ray Diffraction	
Weight of Active Cathode Material	Milli- Equivalents	Discharge Current	Duration of Test	Coulombs Theoret. Actual	Coulombic Efficiency	
A. Cupric Fluoride Filter Pad Cathodes. (Continued)						
7. 0.218 g	4.29	1.4 ± 0.3 ma	810 min.	414.0 101.4	24.4%*	Cu, CuCl
8. 0.252 g	4.96	5 ma	210 min.	478.8 63.0	13.2%	CuF ₂ , graphite
9. 0.237 g	4.67	10.8 ± 0.8 ma	30 min.	450.7 19.4	4.3%	CuCl, CuOHF, graphite
B. Cupric Fluoride Filter Pad Cathodes Containing LiClO ₄ .						
1. 0.216 g	4.25	1.37 ± 0.3 ma	1161 min.	410.1 130.5	31.8%	Cu, Cu ₂ O, LiF, graphite
C. Lead Dioxide Cathodes.						
1. 0.95 g	7.9	10 ma	71 min.	762.4 42.6	5.6%	Not determined
D. Silver Difluoride Cathodes.						
1. 1.03 g	14.2	1.7 ± 0.4 ma	3240 min.	1370.3 330.5	24.1%*	Not determined
2. 0.712 g	9.76	1.9 ± 0.3 ma	2460 min.	945.8 280.4	29.7%	Ag, AgCl
E. Silver Oxide Cathode.						
1. 0.615 g	9.9	9.1 ± 1.3 ma	1560 min.	955.4 853.8	89.4%	Ag

* Test terminated before cut-off voltage of 0.2V for the cell was reached

FIGURE 2. CONSTANT CURRENT* DISCHARGE FOR CELL A-2, LITHIUM VS. CUPRIC FLUORIDE
 FILTER PAD CATHODE** IN 1 MOLAL LiClO_4 -PROPYLENE CARBONATE ELECTROLYTE



* 5 ma

** Cathode area - 1 cm^2

FIGURE 3. % THEORETICAL OPEN CIRCUIT VOLTAGE (FULL CELL) VS. % THEORETICAL COULOMBS FOR CUPRIC FLUORIDE FILTER PAD CATHODES VS. LITHIUM IN LiClO_4 -PROPYLENE CARBONATE ELECTROLYTE.

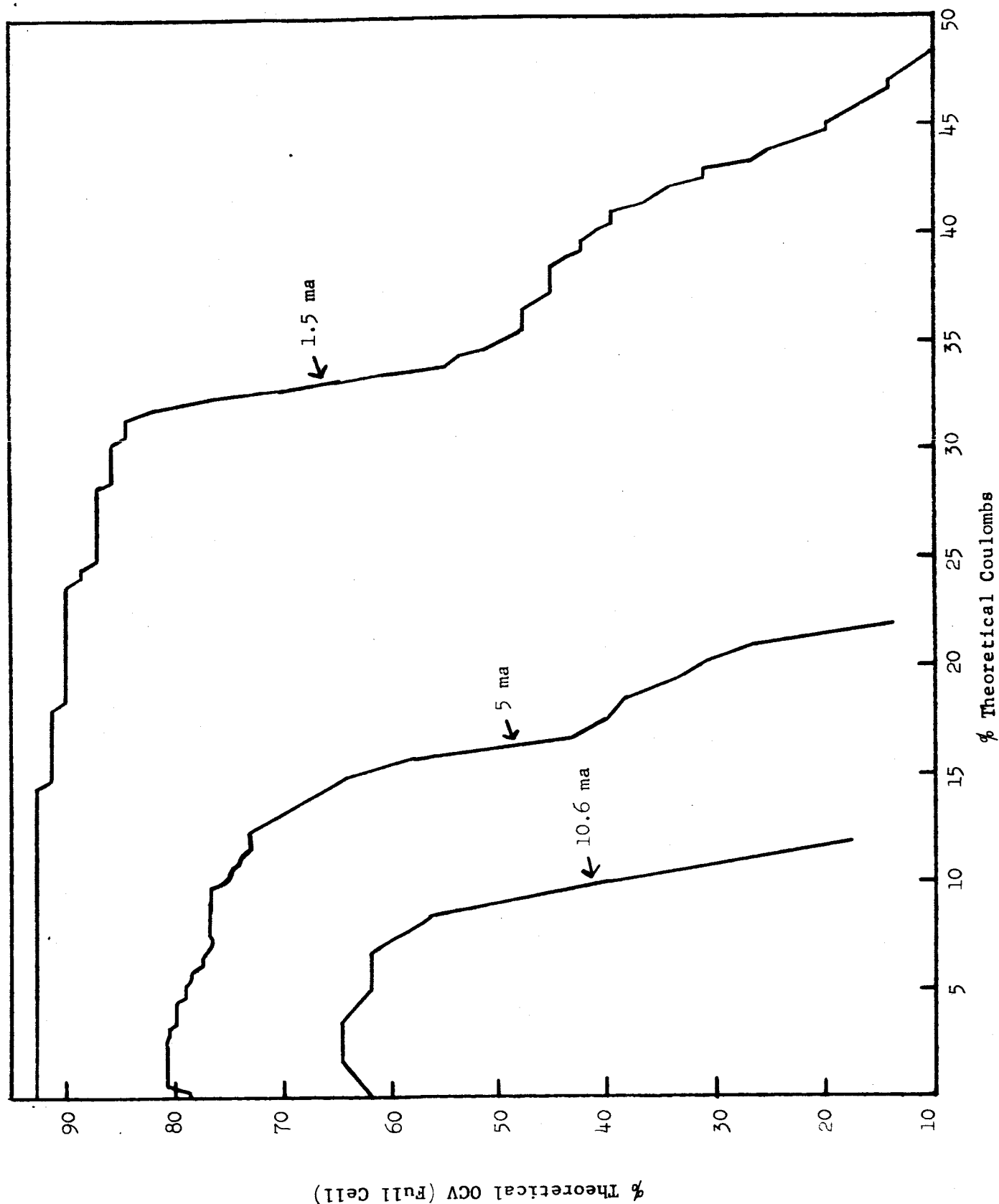


FIGURE 4. % THEORETICAL OPEN CIRCUIT VOLTAGE (FULL CELL) VS. % THEORETICAL COULOMBS FOR CUPRIC FLUORIDE FILTER PAD CATHODES VS. LITHIUM IN N-PHENYL-N,N-TRIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE ELECTROLYTE.

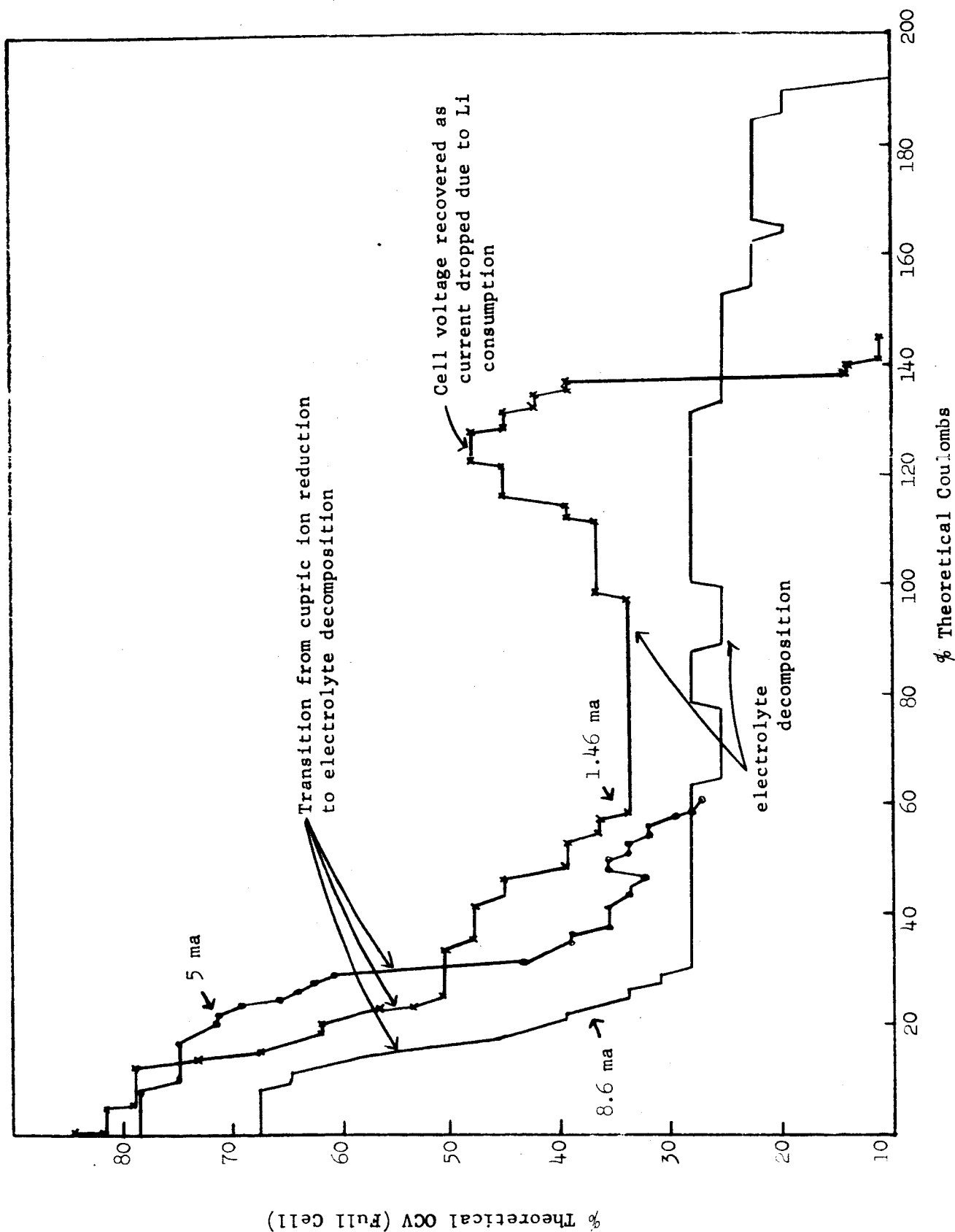


FIGURE 5. % THEORETICAL OPEN CIRCUIT VOLTAGE (FULL CELL) VS. % THEORETICAL COULOMBS FOR
 CUPRIC FLUORIDE FILTER PAD CATHODES VS. MAGNESIUM IN AlCl_3 -ACETONITRILE ELECTROLYTE.

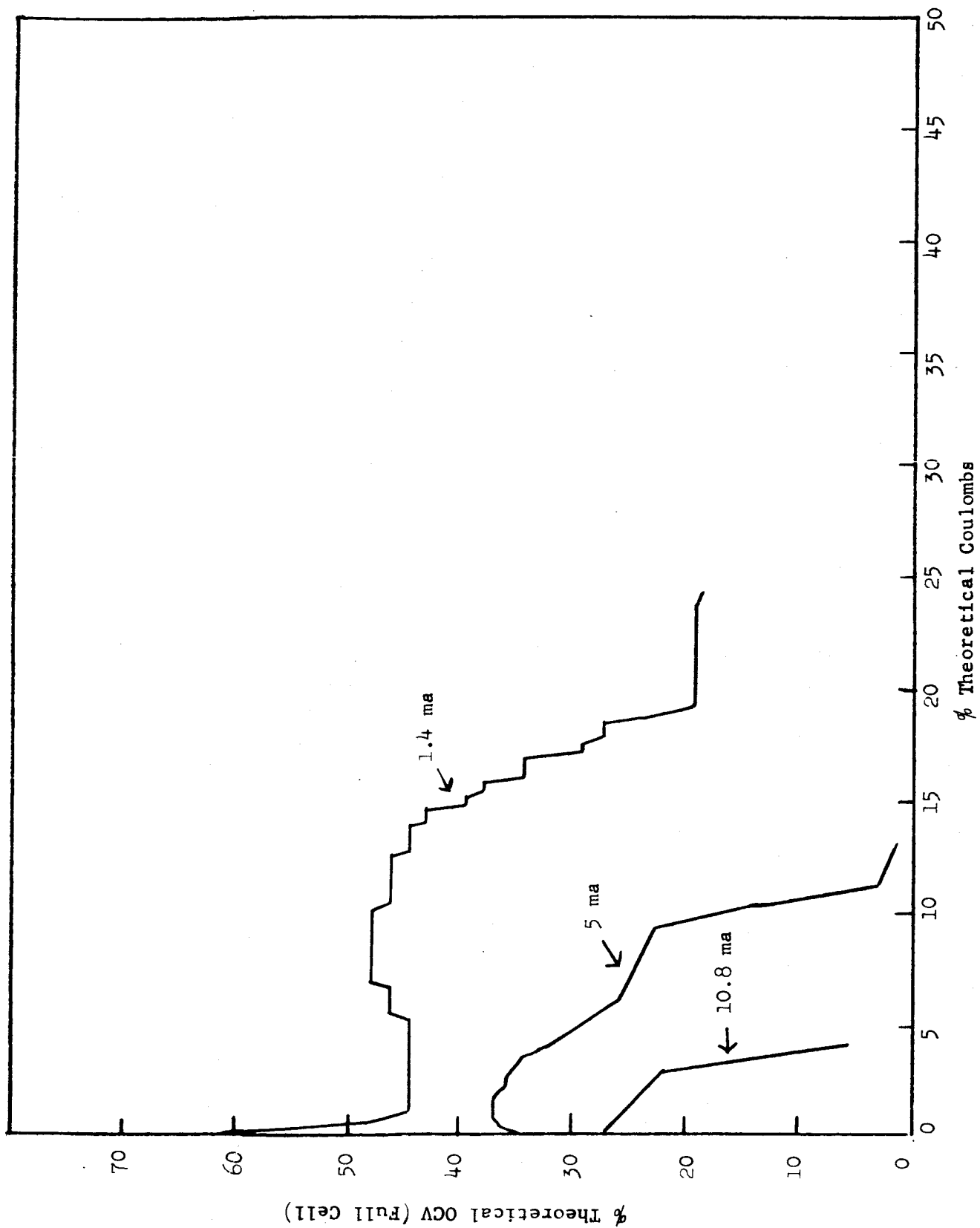


FIGURE 6. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE FILTER PAD CATHODES IN 1 MOLAL LiClO_4 -PROPYLENE CARBONATE ELECTROLYTE. Mg COUNTER ELECTRODE, Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE. CATHODE AREA - APPROXIMATELY 4 mm^2 .

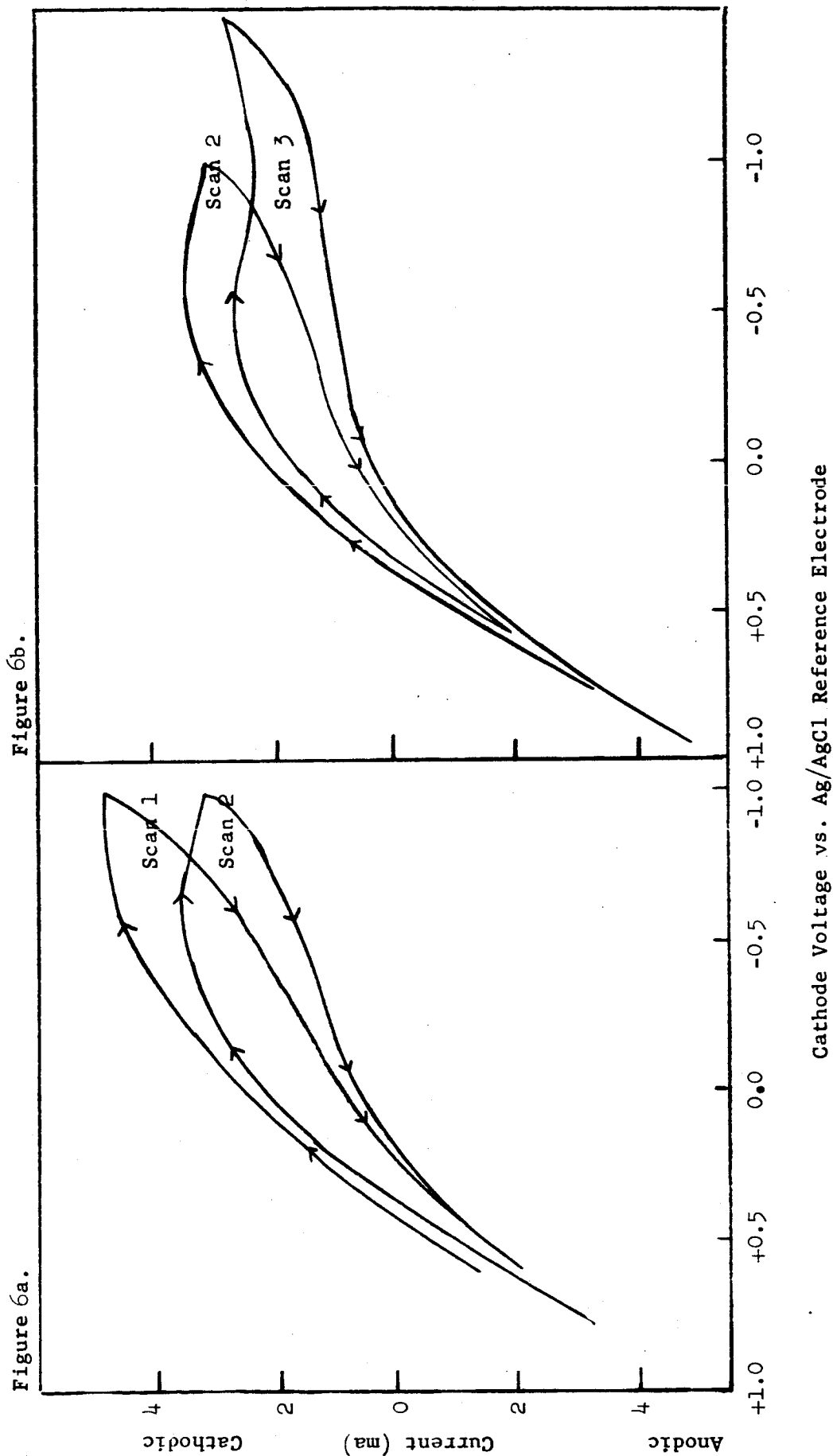


FIGURE 6. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE FILTER PAD CATHODES IN 1 MOLAL LiClO_4 -PROPYLENE CARBONATE ELECTROLYTE. Mg COUNTER ELECTRODE, Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE. CATHODE AREA - APPROXIMATELY 4 mm^2 . (Continued)

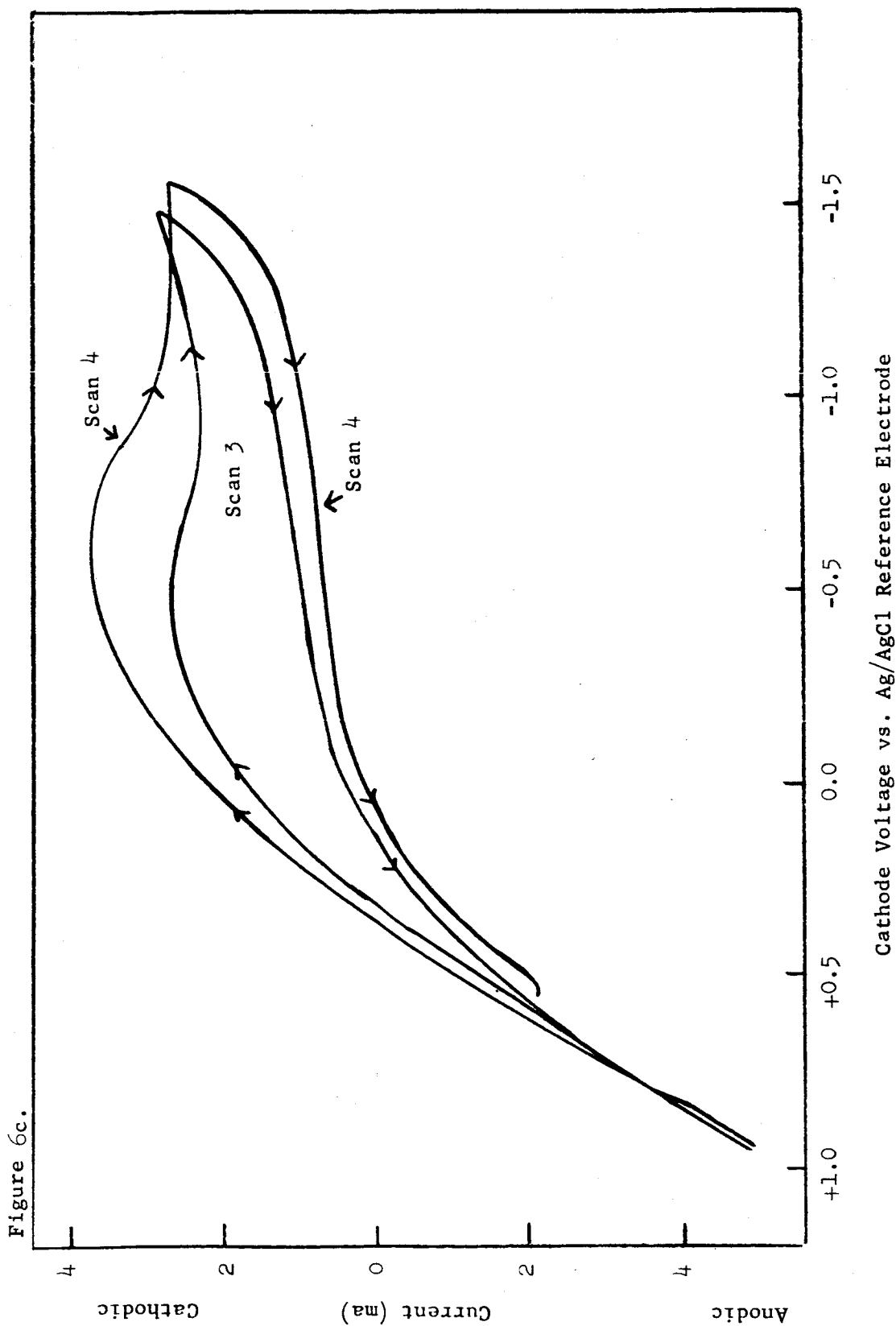


FIGURE 6. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE FILTER PAD CATHODES IN 1 MOLAL LiClO_4 -PROPYLENE CARBONATE ELECTROLYTE. Mg COUNTER ELECTRODE, Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE. CATHODE AREA - APPROXIMATELY 4 mm^2 . (Continued)

Figure 6d.

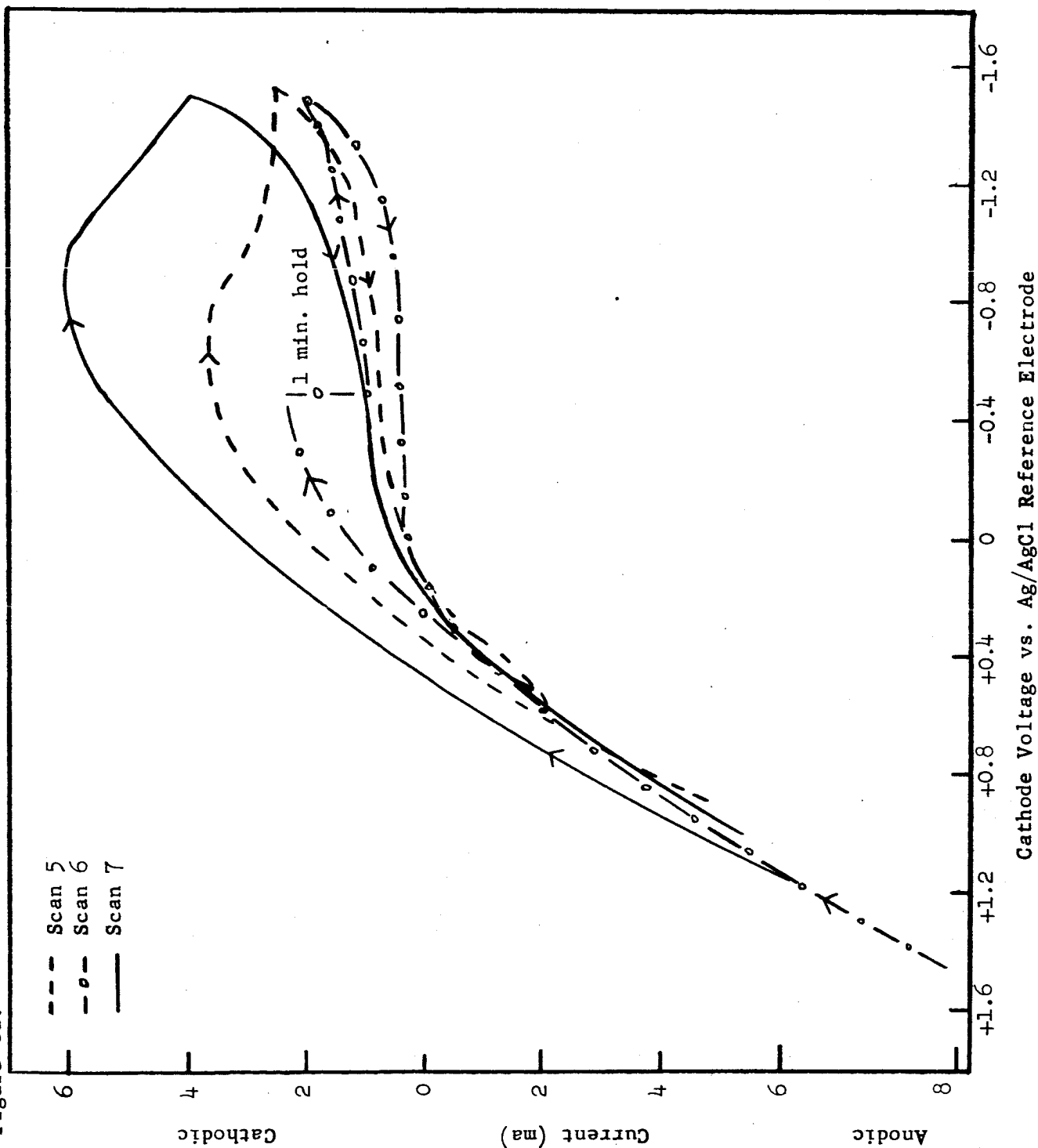


FIGURE 7. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE FILTER PAD CATHODES IN
 1 MOLAL LiClO_4 -PROPYLENE CARBONATE AND 1 MOLAL N-PHENYL N,N,N-TRIMETHYLAMMONIUM
 HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE ELECTROLYTES. Mg COUNTER ELECTRODE, Ag/AgCl
 REFERENCE ELECTRODE. 50 mv/sec SCAN RATE. CATHODE AREA - APPROXIMATELY $\frac{1}{4} \text{ mm}^2$.

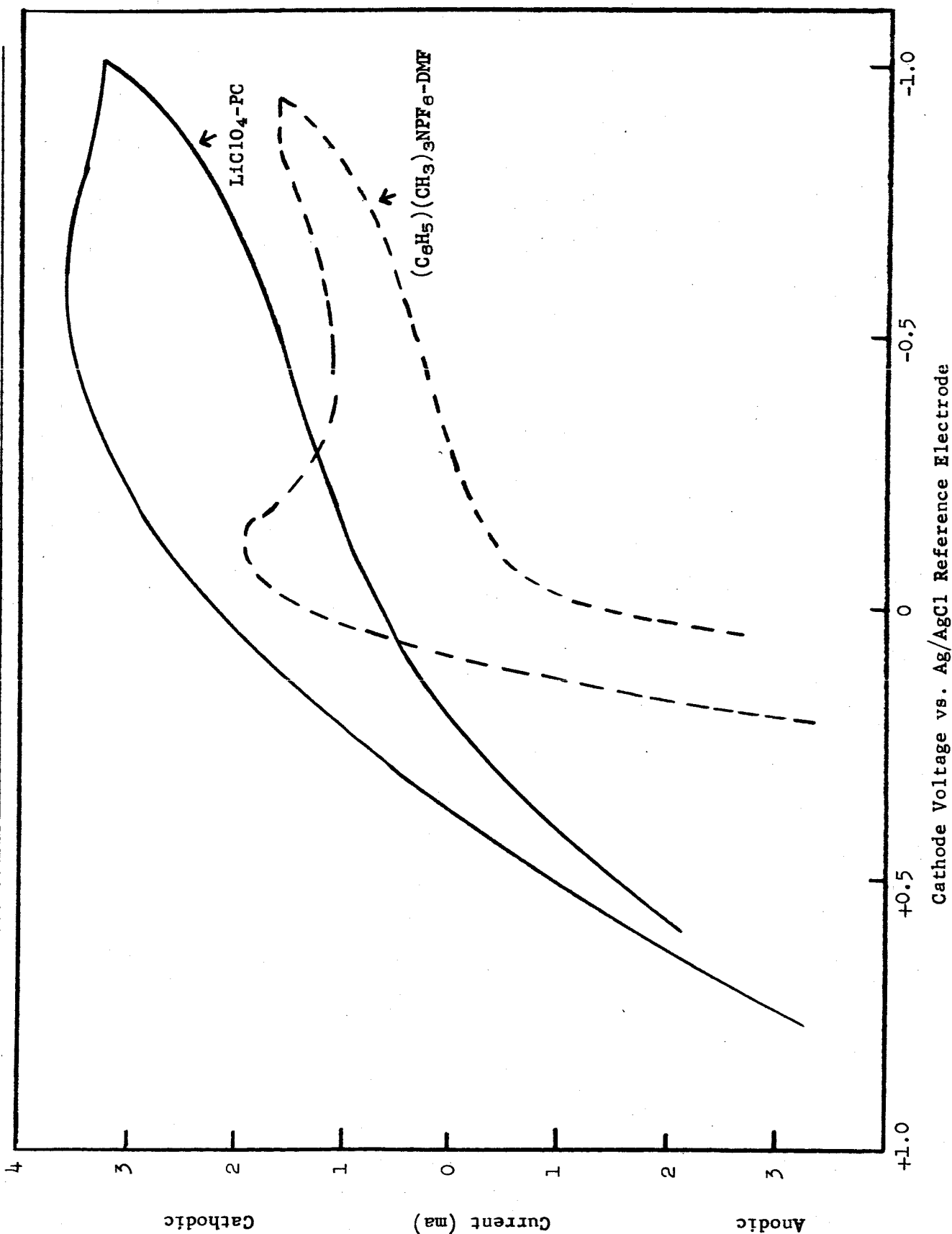


FIGURE 8a.

LINEARLY VARYING POTENTIAL SCANS OF A SILVER OXIDE CATHODE IN 1 MOLAL N-PHENYL-N,N,N-TRIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE ELECTROLYTE. MG COUNTER ELECTRODE. Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE. CATHODE AREA - APPROXIMATELY 1 cm².

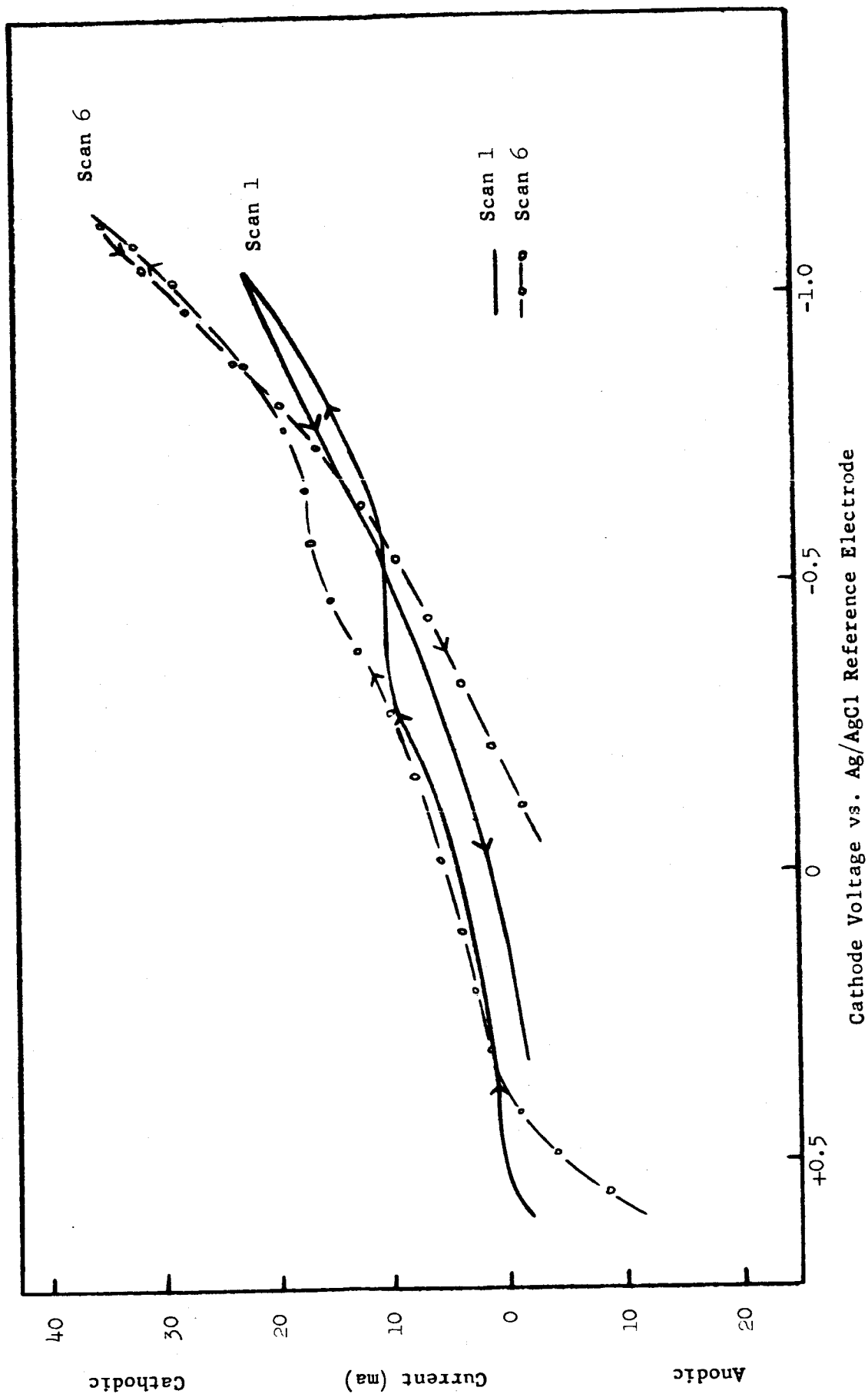


FIGURE 8b.

LINEARLY VARYING POTENTIAL SCANS OF A SILVER OXIDE CATHODE IN 1 MOLAL N-PHENYL-N,N-TRIMETHYLANMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE ELECTROLYTE. Mg COUNTER ELECTRODE. Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE. CATHODE AREA - APPROXIMATELY 1 cm².

(Continued)

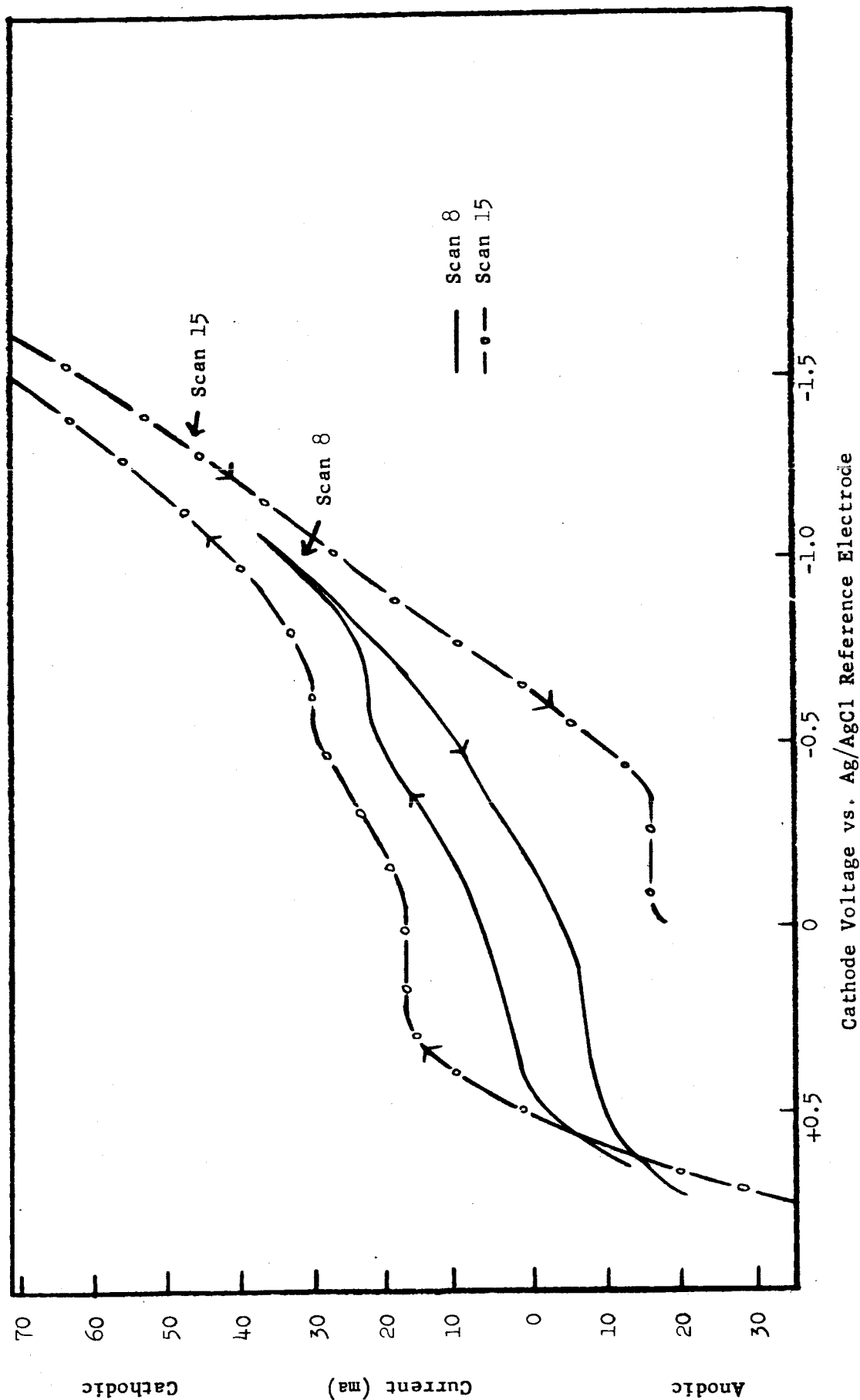


TABLE V. DATA GIVEN BY MOREHOUSE AND GLICKSMAN* ON
ORGANIC CATHODE MATERIALS IN AQUEOUS SOLUTIONS

Compound	Voltage of Discharge Plateau	Capacity ** (amp-min/g)		% Efficiency	Discharge Rate (amp/g)
		Theoretical	Actual		
N-chlorosuccinimide	+0.70	24.1	11.7	48.5	0.030
m-dinitrobenzene	-0.20	114.9	88.5	77	0.005
2,4-dinitrophenol	-0.15 to -0.22	***	***	***	0.030
p-nitroaniline	-0.32	69.9	61	87	0.005
4-nitrosophenol	0.00	52.2	48.2	92.3	0.005
p-quinonedioxime	-0.10	69.9	65.2	93.3	0.005

* R. Glicksman and C. K. Morehouse, J. Electrochem. Soc., 104, 467 (1957); 105, 299, 619 (1958);
106, 288 (1959).

** Multiply $\frac{453.4\text{g/lb}}{60\text{ min/hr}}$ x capacity (amp-min/g) = amp-hrs/lb

*** Not available.

FIGURE 9. LINEARLY VARYING POTENTIAL SCANS OF 0.1 MOLAL N-CHLOROSUCCINIMIDE IN 1 MOLAL LiPF_6 -DIMETHYLFORMAMIDE AND 1 MOLAL LiPF_6 -N-NITROSODIMETHYL-AMINE ELECTROLYTES. HP-15 CARBON (1 cm^2) WORKING AND COUNTER ELECTRODES. Ag/AgCl Reference Electrode. 50 mv/sec scan rate.

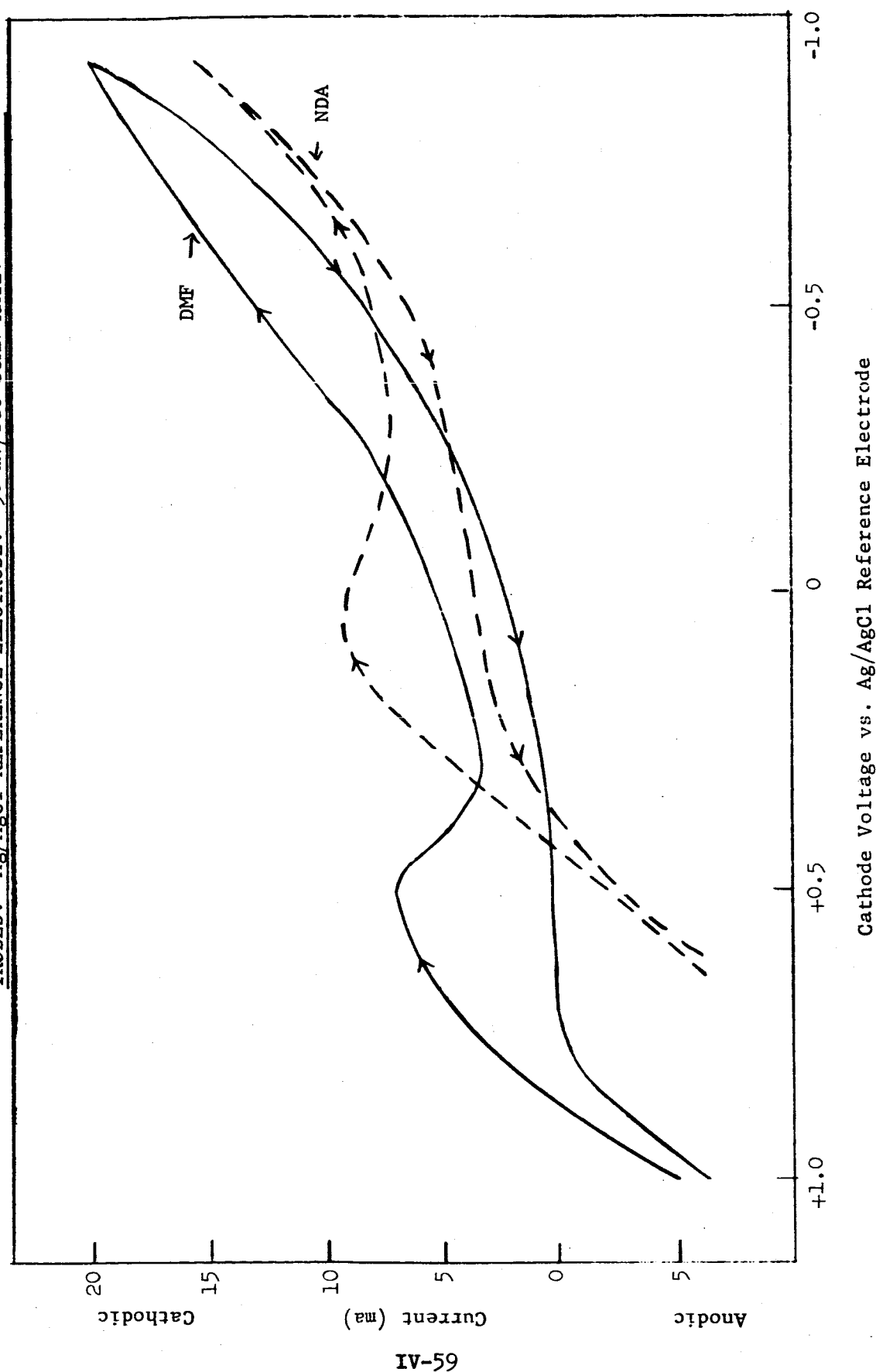


FIGURE 10. LINEARLY VARYING POTENTIAL SCANS OF 0.1 MOLAL META-DINITROBENZENE IN 1 MOLAL LiPF_6 -DIMETHYLFORMAMIDE AND 1 MOLAL LiPF_6 -N-NITROSODIMETHYL-AMINE ELECTROLYTES. HP-15 CARBON (1 cm^2) WORKING AND COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE.

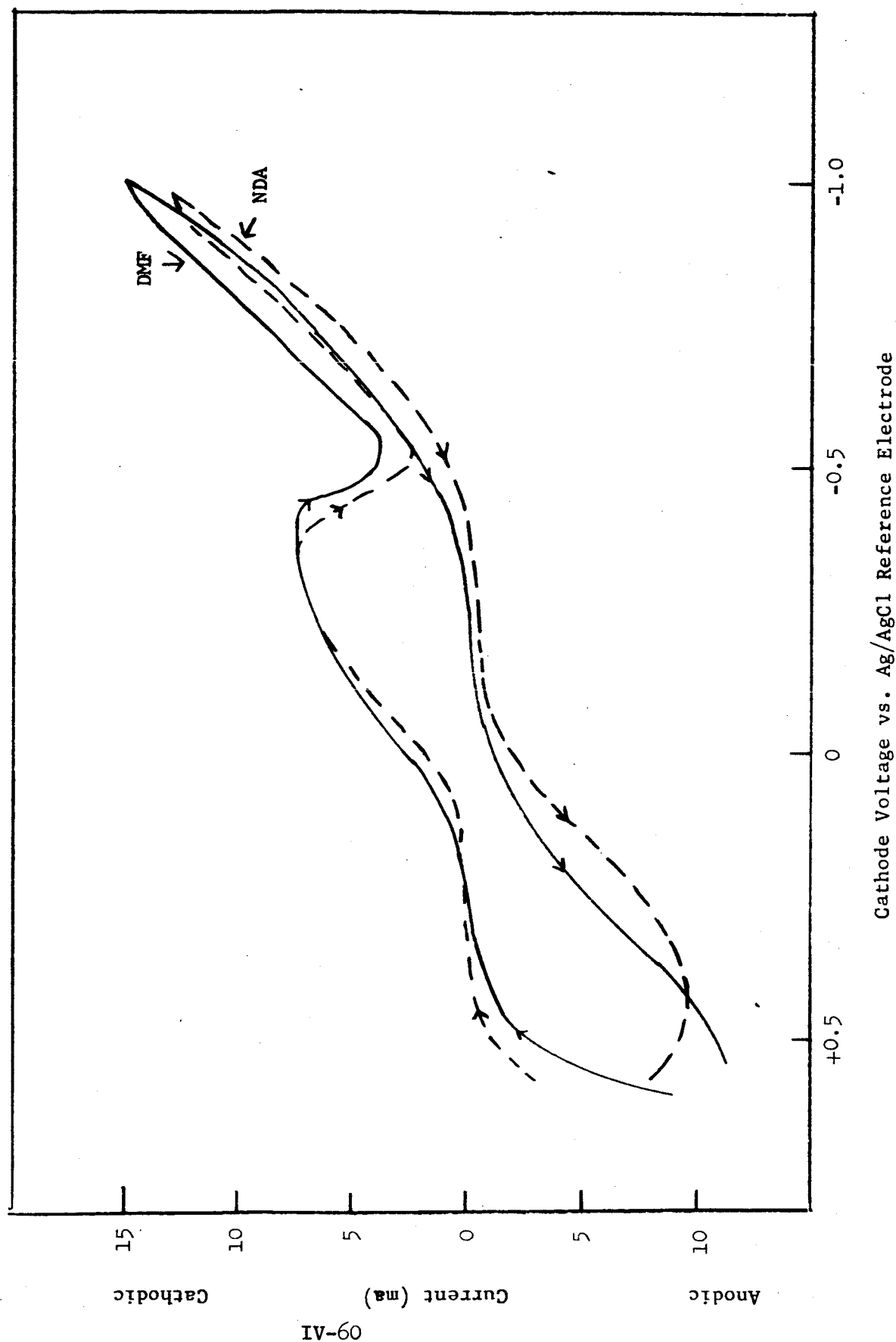


FIGURE 11. LINEARLY VARYING POTENTIAL SCANS OF 0.1 MOLAL N-CHLOROSUCCINIMIDE AND 0.1 MOLAL META-DINITROBENZENE IN 1 MOLAL LiPF₆-DIMETHYLFORMAMIDE ELECTROLYTE. HP-15 CARBON (1 cm²) WORKING AND COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE.

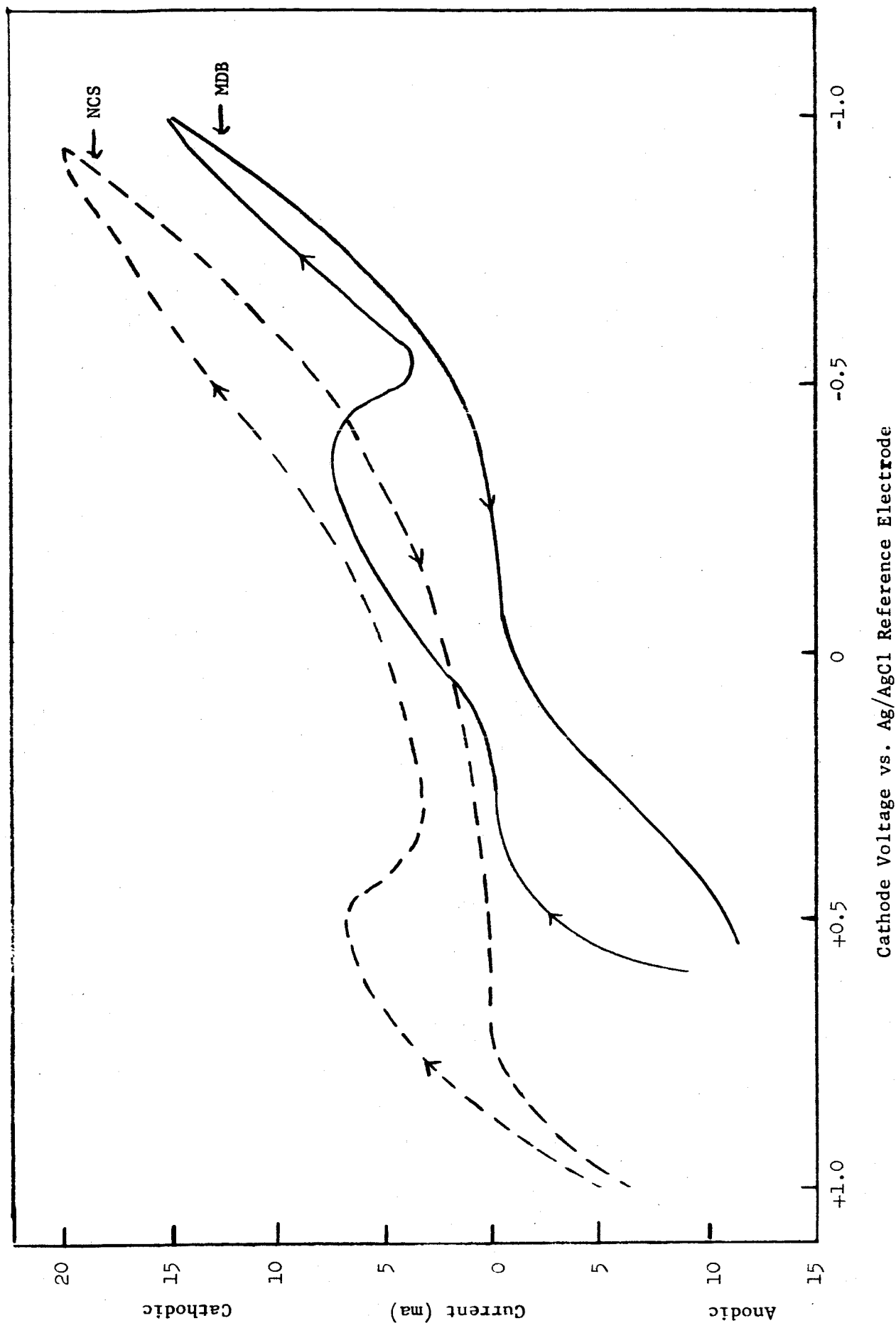


FIGURE 12. LINEARLY VARYING POTENTIAL SCANS OF 0.1 MOLAL 4-NITROSOPHENOL AND 0.1 MOLAL 2,4-DINITROPHENOL IN 1 MOLAL LiPF_6 -DIMETHYLFORMAMIDE ELECTROLYTE. HP-15 CARBON (1 cm^2) WORKING AND COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE.

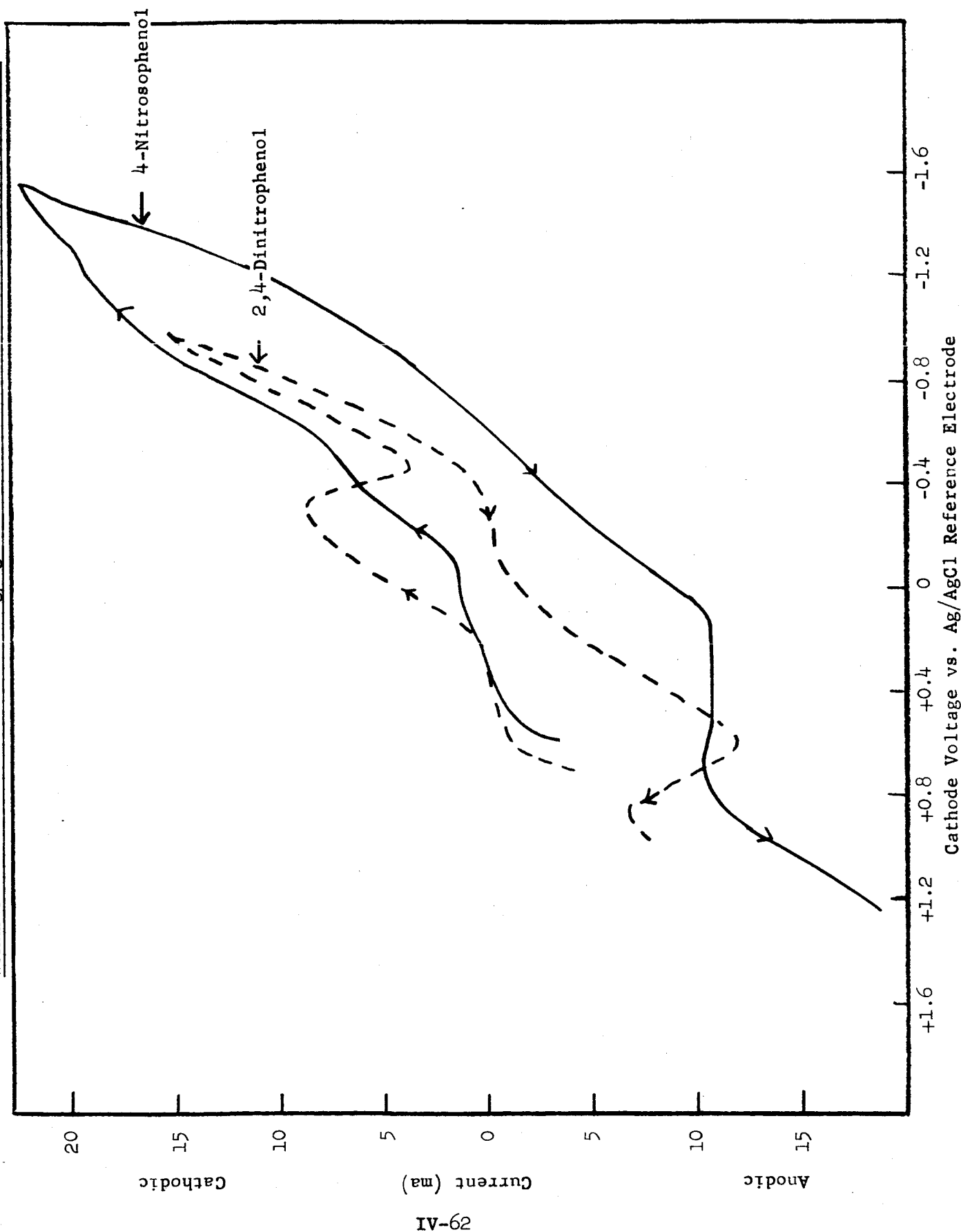


FIGURE 13. LINEARLY VARYING POTENTIAL SCANS OF 1 MOLAL PICRIC ACID IN 1 MOLAL N-PHENYL N,N,N-TRIMETHYL-AMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE ELECTROLYTE AND 0.1 MOLAL PARA-QUINONEDIOXIME IN 1 MOLAL LiPF₆-DIMETHYLFORMAMIDE. HP-15 CARBON (1 cm²) WORKING AND COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODE. 30 mv/sec SCAN RATE FOR PICRIC ACID. 50 mv/sec SCAN RATE FOR PARA-QUINONEDIOXIME.

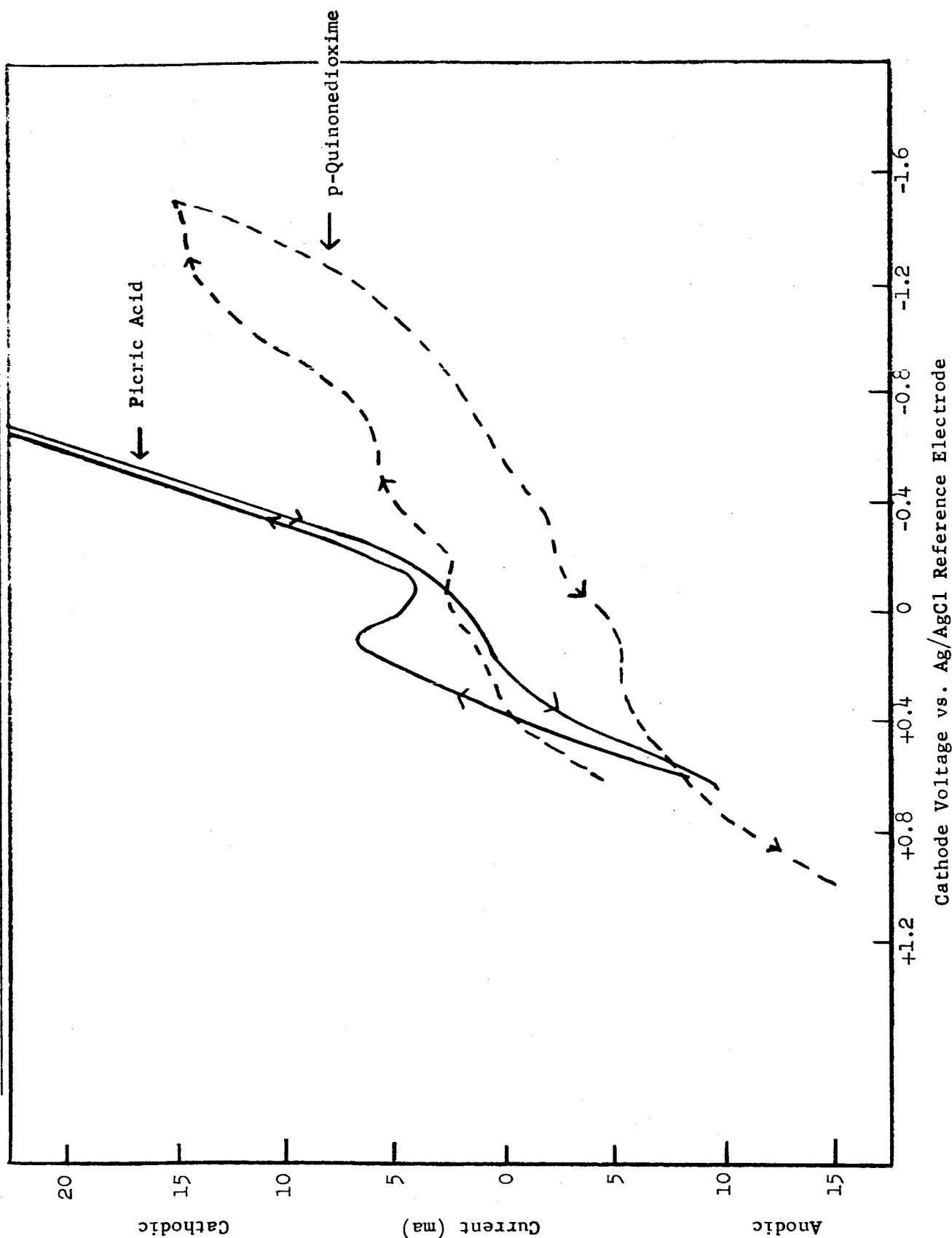


TABLE VI. DISCHARGE OF CELLS UTILIZING m-DINITROBENZENE
AS THE ACTIVE ORGANIC CATHODE MATERIAL

	<u>Page</u>
A. <u>Magnesium-m-Dinitrobenzene in Acetonitrile.</u>	
1. Porous HP-10 speer carbon container.....	IV-65
2. Porous HP-15 speer carbon container.....	IV-66
3. Porous HP-20 speer carbon container.....	IV-68
B. <u>Lithium-m-Dinitrobenzene</u>	IV-69

TABLE VI. DISCHARGE OF CELLS UTILIZING m-DINITROBENZENE
AS THE ACTIVE ORGANIC CATHODE MATERIAL

A. Magnesium-m-Dinitrobenzene.

1. Anode - magnesium. Area - 1 cm².

Cathode - 1 ml of 1 molal m-dinitrobenzene-acetonitrile was placed in a porous HP-10 Speer carbon container. The carbon container was 1x1x4.5 cm with a 0.2 cm² hole bored 4 cm into one end. The filled container was immersed 2 cm in the electrolyte and had an approximate surface area of 8 cm².

Electrolyte - 1 molal $O \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}_2\text{PF}_6$ (morpholinium hexafluorophosphate)-acetonitrile.

Reference electrode - Ag/AgCl.

Time (Minutes)	Cell Voltage	Cathode Voltage (vs. Ag/AgCl Reference Electrode)	Current (ma)	Observations
0	----	----	0	
3	1.01	-0.14	0	An additional 1 ml of 1 molal m-dinitrobenzene-acetonitrile was added.
6	0.95	-0.13	0	
7	0.86	-0.22	2	
10	0.79	-0.31	2	
23	0.71	-0.38	2	The solution became slightly turbid and yellow.
50	0.66	-0.42	2	
72	0.63	-0.44	2	Yellow crystals formed around the rim of the carbon container and a yellow-white precipitate formed in solution.
115	0.61	-0.47	2	
123	0.59	-0.48	2	
124	0.44	-0.57	10	The solution became deeper yellow in color and more yellow solid formed on the faces of the carbon container.
131	0.44	-0.61	10	
147	0.43	-0.62	10	
150	0.66	-0.45	0	At the end of the discharges the magnesium anode was partially covered with a black film. The carbon container seemed to be covered with a thin gelatinous film and yellow crystals surrounded the rim. The electrolyte was a turbid yellow and a white precipitate had formed in solution. There was no change in the reference electrode.

TABLE VI. DISCHARGE OF CELLS UTILIZING m-DINITROBENZENE
AS THE ACTIVE ORGANIC CATHODE MATERIAL (Continued)

A. Magnesium-m-Dinitrobenzene. (Continued)

2. Anode - magnesium. Area - 1 cm².

Cathode - 3.94 g. m-dinitrobenzene was dissolved in 30 ml of acetonitrile (1 molal). 1 ml of this solution was placed in a porous HP-15 Speer carbon container. The carbon container was 1x1x3.8 cm with a 0.2 cm² hole bored 3.3 cm into one end. The filled container was immersed 2 cm in the electrolyte and had an approximate surface area of 8 cm².

Electrolyte - 1 molal $O\begin{matrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{matrix} \text{NH}_2\text{PF}_6$ (morpholinium hexafluorophosphate)-acetonitrile.

Reference electrode - Ag/AgCl.

Time (Minutes)	Cell Voltage	Cathode Voltage (vs. Ag/AgCl Reference Electrode)	Current (ma)	Observations
0	1.46	+0.25	0	
2	1.32	+0.13	0	
3	1.00	-0.10	2	
4	0.96	-0.21	2	
7	0.91	-0.27	2	
12	0.86	-0.32	2	
16	0.84	-0.34	2	
17	0.68	-0.42	10	
19	0.64	-0.50	10	
25	0.58	-0.54	10	Yellow crystals appeared at the rim of the carbon container. The solution became slightly turbid and the magnesium turned partially black.
37	0.52	-0.59	10	
49	0.48	-0.63	10	
61	----	-0.60	10	
72	0.51	-0.58	10	Solution turning yellow. Crystal formation continued.
86	0.51	-0.57	10	
107	0.50	-0.58	10	
143	0.45	-0.60	10	
183	0.42	-0.63	10	

TABLE VI. DISCHARGE OF CELLS UTILIZING m-DINITROBENZENE
AS THE ACTIVE ORGANIC CATHODE MATERIAL (Continued)

A. Magnesium-m-Dinitrobenzene. (Continued)

No. 2 - Continued

<u>Time</u> <u>(Minutes)</u>	<u>Cell</u> <u>Voltage</u>	<u>Cathode Voltage</u> <u>(vs. Ag/AgCl</u> <u>Reference Electrode)</u>	<u>Current</u> <u>(ma)</u>	<u>Observations</u>
236	0.40	-0.66	10	Solution changed from yellow to brown.
259	0.38	-0.68	10	
284	0.35	-0.69	10	
323	0.31	-0.75	10	
331	0.30	-0.75	10	
345	0.79	-0.42	0	After the discharge the anode was covered with a thin black film. The cathode was covered with a white gelatinous substance. A slight amount of yellow solid surrounded the top of the carbon container. The electrolyte was turbid brown and a yellow precipitate was present in solution.

TABLE VI. DISCHARGE OF CELLS UTILIZING m-DINITROBENZENE
AS THE ACTIVE ORGANIC CATHODE MATERIAL (Continued)

A. Magnesium-m-Dinitrobenzene. (Continued)

3. Anode - magnesium. Area - 1 cm².

Cathode - 1 ml of 1 molal m-dinitrobenzene-acetonitrile was placed in a porous HP-20 Speer carbon container. The carbon container was 1x1x3 cm with a 0.2 cm² hole bored 2.5 cm into one end. The filled container was immersed 2 cm in the electrolyte and had an approximate surface area of 8 cm².

Electrolyte - 1 molal $O\begin{matrix} CH_2CH_2 \\ CH_2CH_2 \end{matrix}NH_2PF_6$ (morpholinium hexafluorophosphate)-acetonitrile.

Reference electrode - Ag/AgCl.

<u>Time</u> <u>(Minutes)</u>	<u>Cell</u> <u>Voltage</u>	<u>Cathode Voltage</u> <u>(vs. Ag/AgCl</u> <u>Reference Electrode)</u>	<u>Current</u> <u>(ma)</u>	<u>Observations</u>
0	1.40	+0.10	0	
1	1.08	-0.12	0	Slight amount of gassing at the cathode.
3	1.04	-0.14	0	
4	0.95	-0.20	2	
7	0.89	-0.26	2	
8	0.74	-0.36	10	
9	0.66	-0.46	10	
17	0.57	-0.52	10	
26	0.53	-0.53	10	Yellow solid formed on the carbon container. The solution appeared turbid.
50	0.50	-0.54	10	
69	0.48	-0.55	10	Two liquid phases formed. The upper layer was turbid yellow. The lower layer was clear.
125	0.45	-0.57	10	
1020*	0.70	-0.29	0	After the discharge the magnesium was completely consumed. The part of the carbon container exposed to the electrolyte had turned gray. The solution consisted of a dark brown upper layer and a gray-brown lower layer which contained a large amount of suspended solid material.

* The cell was allowed to discharge overnight.

TABLE VI. DISCHARGE OF CELLS UTILIZING m-DINITROBENZENE
AS THE ACTIVE ORGANIC CATHODE MATERIAL (Continued)

B. Lithium-m-Dinitrobenzene.

Anode - lithium. Area - 1 cm².

Cathode - 0.59 g. m-dinitrobenzene were packed in a porous HP-15 speer carbon container. The carbon container was 1x1x3.8 cm with a 0.2 cm² hole bored 3.3 cm into one end. The filled container was immersed 2 cm in the electrolyte and had an approximate surface area of 8 cm².

Electrolyte - 1 molal LiPF₆-N-nitrosodimethylamine.

Reference electrode - Ag/AgCl

<u>Time</u> <u>(Minutes)</u>	<u>Cell</u> <u>Voltage</u>	<u>Cathode Voltage</u> <u>(vs. Ag/AgCl</u> <u>Reference Electrode)</u>	<u>Current</u> <u>(ma)</u>	<u>Observations</u>
0	3.20	+0.20	0	
2	3.08	0.00	0	
4	3.04	-0.14	0	
5	2.72	-0.23	2	
8	2.55	-0.51	2	
13	2.72	-0.56	2	
23	2.55	-0.65	2	Lithium changed from dull gray to a bright metallic color.
38	2.50	-0.73	2	
56	2.52	-0.76	2	Vigorous gassing began at the lithium anode.
59	2.23	-0.90	10	
69	2.16	-0.97	10	Gassing evident at both electrodes.
93	2.13	-0.87	10	
106	2.13	-0.86	10	
140	2.17	-0.76	10	Clear solution began to turn orange.
203	0.05	-0.65	4	Lithium electrode broke off and was replaced.
206	2.43	-0.45	0	
215	2.78	-0.33	0	
222	2.82	-0.31	0	
222	2.48	-0.40	10	
226	2.16	-0.66	10	
237	1.60	-0.68	10	
244	2.81	-0.35	0	
247	----	----	10	
250	2.13	-0.71	10	
253	1.92	-0.72	10	
315	2.78	-0.20	0	

TABLE VII. SPECIFICATIONS FOR SPEER CARBONS
USED IN ELECTROCHEMICAL TESTING OF
DISSOLVED ACTIVE CATHODE MATERIALS

Porosity Data

Pore Volume cc/gm

<u>Grade No.</u>	<u>Total</u>	<u>d > 100 μ</u>	<u>100 μ > d 0.06 μ</u>	<u>d < 0.06 μ</u>
HP-10	0.394	0.251	0.066	0.077
HP-15	0.339	0.123	0.155	0.061
HP-20	0.327	0.063	0.195	0.069

Air and Water Permeability

<u>Grade No.</u>	<u>Air Permeability*</u> <u>Ft.³/min. per ft.² of Material</u>	<u>Water Permeability**</u> <u>Gal./min. per ft.² of Material</u>
HP-10	5	12
HP-15	1	3
HP-20	0.7	0.5

* Nitrogen pressure - 2 in. H₂O. Test specimen 1 inch thick.

** 5 lbs./in.² H₂O pressure. Test specimen 1 inch thick.

TABLE VIII. DISCHARGE OF CELLS UTILIZING AN ION EXCHANGE MEMBRANE SEPARATOR

A. Lithium/Cuprous Chloride-Cupric Chloride.

Anode - lithium.

Cathode - 25 wt. % CuCl_2 , 75 wt. % Cu_2Cl_2 fused onto nickel expanded metal. Area = 1cm^2 .

Electrolyte - 1 molal LiClO_4 -propylene carbonate.

Reference electrodes - Ag/AgCl.

Anion exchange membrane - (E-5451-1/2 Ionics Inc.) The membrane had a Dynel backing. Specific conductance of the membrane ranged from $4 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in 0.01 N NaCl to $30 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in 3.0 N NaCl. Bulletin No. AR111.1 (1964), Ionics Inc., Cambridge, Mass.

Cell construction - The anion exchange membrane was placed between two blocks of Plexiglas and the blocks were bolted together so that a $2 \times 2 \times 2 \text{ cm}$ well was placed on each side of the membrane.

Time (Minutes)	Cell Voltage	Anode Voltage (vs. Ag/AgCl Reference Electrode*)	Cathode Voltage (vs. Ag/AgCl Reference Electrode**)	Anode Reference Electrode vs. Cathode Reference Electrode	Current (ma)
0	3.10	-2.75	+0.14	+0.04	0
5	0.65	-2.64	-1.26	----	5
9	0.62	-2.67	-1.24	+0.84	5
14	0.76	-2.71	-1.06	----	5
24	0.80	-2.75	-0.94	+1.06	5

The anode and cathode were moved closer together at this point and a greater amount of lithium surface area was exposed to the electrolyte.

35	0.92	-2.76	-0.88	+1.00	5
47	0.86	-2.76	-0.85	+1.08	5
84	2.00	-2.83	-0.33	+0.53	2
102	2.75	-2.92	-0.18	+0.02	0

Observations: The dark green solution of cathode material in propylene carbonate had turned red-brown. The Plexiglas was attacked.

* Located in the anolyte

** Located in the catholyte

TABLE VIII. DISCHARGE OF CELLS UTILIZING AN ION EXCHANGE MEMBRANE SEPARATOR (Continued)

B. Lithium/Cupric Chloride.

1. Anode - lithium. Area - 2 cm^2 .

Active cathode material - saturated $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -propylene carbonate.

Cathodic current collector - copper metal. Area = 2 cm^2 .

Anolyte - 1 molal LiClO_4 -propylene carbonate.

Reference electrodes - Ag/AgCl.

Anion exchange membrane - (E-5451-1/2 Ionics Inc.) The membrane had a Dynel backing. Specific conductance of the membrane ranged from $4 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in 0.01 N NaCl to $30 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in 3.0 N NaCl. Bulletin No. AR111.1 (1964), Ionics Inc., Cambridge, Mass.

Cell construction - The anion exchange membrane was placed between two blocks of Plexiglas and the blocks were bolted together so that a $2 \times 2 \times 2 \text{ cm}$ well was placed on each side of the membrane.

<u>Time (Minutes)</u>	<u>Cell Voltage</u>	<u>Anode Voltage (vs. Ag/AgCl Reference Electrode*)</u>	<u>Cathode Voltage (vs. Ag/AgCl Reference Electrode**)</u>	<u>Anode Reference Electrode vs. Cathode Reference Electrode</u>	<u>Current (ma)</u>
0	3.12	-3.05	+0.17	+0.12	0
8	1.47	-2.07	+0.07	+0.70	5
13	1.42	-2.08	+0.06	+0.77	5
27	1.23	-2.12	+0.03	+0.97	5
45	0.95	-2.13	+0.01	+1.25	5
69	0.73	-2.13	0.00	+1.43	5
81	0.59	-2.07	-0.04	+1.48	5
85	2.96	-3.00	+0.07	+0.08	0

Observations: At the end of the discharge the copper screen remained unchanged. The reference electrode in the catholyte had turned brown. The dark green catholyte remained unchanged in color. The membrane was red-brown on the side facing the cathode.

* Located in the anolyte

** Located in the catholyte

TABLE VIII. DISCHARGE OF CELLS UTILIZING AN ION EXCHANGE MEMBRANE SEPARATOR (Continued)

B. Lithium/Cupric Chloride.

2. Anode - lithium. Area = ca. 0.2cm^2 .

Active cathode material - 1 molal $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ -DMF saturated with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

Cathodic current collector - copper metal. Area = ca. 0.2cm^2 .

Electrolyte - 1 molal $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6^*$ -DMF.

Reference electrodes - Ag/AgCl.

Anion exchange membrane - (E-5451-1/2, Ionics Inc.) The membrane had a Dynel backing. Specific conductance of the membrane ranged from $4 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in 0.01 N NaCl to $30 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in 3.0 N NaCl. Bulletin AR111.1 (1964), Ionics Inc., Cambridge, Mass.

Cell construction - The anion exchange membrane was placed between two blocks of polypropylene and the blocks were bolted together so that a $1 \times 1 \times 1 \text{ cm}$ well was placed on each side of the membrane.

Time (Minutes)	Cell Voltage	Anode Voltage (vs. Ag/AgCl Reference Electrode**)	Cathode Voltage (vs. Ag/AgCl Reference Electrode***)	Anode Reference Electrode vs. Cathode Reference Electrode	Current (ma)
0	3.0	-3.0	-0.07	----	0.0
0	2.4	-2.6	-0.13	-0.17	2.1
10	2.4	-2.7	-0.14	+0.11	2.1
20	2.4	-2.7	-0.14	+0.05	2.1
30	2.4	-2.6	-0.14	+0.04	2.1
40	2.4	-2.6	-0.15	+0.31	2.1
50	1.8	-2.4	-0.16	----	4.7
60	1.8	-2.4	-0.17	+0.29	4.6
70	1.8	-2.4	-0.18	+0.28	4.6
80	1.8	-2.4	-0.20	+0.31	4.6
90	1.7	-2.4	-0.22	+0.33	4.6
100	0.14	-2.1	-1.1	+0.89	8.2
110	0.17	-2.2	-0.9	+1.04	9.2
120	1.5	-2.5	-0.4	+1.18	4.8
125	2.3	-2.7	-0.2	+0.64	1.8
125	3.0	-2.9	-0.04	-0.15	0.0

Observations: The original electrolyte was colorless and clear. Addition of CuCl_2 to the catholyte gave it a dark green color. During the 10 ma discharge the anolyte started to turn light green. At the end of the test, the lithium anode was black and the anolyte had a green tint. The catholyte appeared unchanged.

* N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate.

** Located in the anolyte.

*** Located in the catholyte.

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS

Tests of Two Weeks Duration.

Page

A. Stability in Acetonitrile Solutions. IV-75

<u>Solute</u>	<u>Anode Material</u>
1. $(\text{CH}_3)_4\text{NPF}_6$ - (Tetramethylammonium hexafluorophosphate)	Ca Mg
2. $(n\text{-C}_3\text{H}_7)_4\text{NPF}_6$ - (Tetra-n-propylammonium hexafluorophosphate)	Mg
3. $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ - (N-phenyl-N,N,N-trimethylammonium hexafluorophosphate)	Mg

B. Stability in N,N-Dimethylformamide Solutions. IV-76

1. KPF_6	Li
2. $(\text{CH}_3)_4\text{NPF}_6$	Li

C. Stability in Ethylene Carbonate (80 Wt. %)-
Propylene Carbonate (20 Wt. %) Solutions. IV-77

1. AlCl_3	Ca Li Mg
2. $(\text{CH}_3)_4\text{NPF}_6$	Ca Li Mg
3. $(n\text{-C}_3\text{H}_7)_3\text{NHAsF}_6$ - (Tri-n-propylammonium hexafluoroarsenate)	Li
4. $\text{O} \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}_2\text{PF}_6$ - (Morpholinium hexafluorophosphate)	Li

D. Stability in N-Nitrosodimethylamine Solutions. IV-80

1. AlCl_3	Ca Mg
2. KPF_6	Li Mg
3. MgCl_2	Mg
4. $(\text{CH}_3)_4\text{NPF}_6$	Ca Li Mg
5. $(n\text{-C}_3\text{H}_7)_4\text{NPF}_6$	Mg
6. $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$	Ca Li Mg

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS

Tests of Two Weeks Duration.

A. Stability in Acetonitrile Solutions.

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
1. $(\text{CH}_3)_4\text{NPF}_6$ (Tetramethyl-ammonium hexa-fluorophosphate)	Ca	Before Exposure	1.1082	1.14×10^{-2} (24°C)	1.14×10^{-2} (24°C)	No change in the appearance of the calcium. A slight amount of fluffy white solid appeared at the bottom of the solution.
		After Two Weeks	1.1100	1.12×10^{-2} (25°C)	1.12×10^{-2} (25°C)	
	Mg	Before Exposure	0.4685	1.14×10^{-2} (24°C)	1.14×10^{-2} (24°C)	Several white spots appeared on the magnesium surface. A slight amount of fluffy white solid appeared at the bottom of the solution.
		After Two Weeks	0.4741	1.13×10^{-2} (25°C)	1.12×10^{-2} (25°C)	
2. $(\text{n-C}_3\text{H}_7)_4\text{NPF}_6$ (Tetra-n-propyl-ammonium hexa-fluorophosphate)	Mg	Before Exposure	0.3900	3.66×10^{-2} (24°C)	3.66×10^{-2} (24°C)	The original brown solution became lighter and a white precipitate appeared. A thin white film formed on the magnesium surface.
		After Two Weeks	0.4082	3.62×10^{-2} (25°C)	3.68×10^{-2} (25°C)	
3. $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ (N-phenyl-N,N-trimethylammonium hexafluorophosphate)	Mg	Before Exposure	0.4249	3.77×10^{-2} (24°C)	3.72×10^{-2} (24°C)	Light gassing occurred on immersion. A white gelatinous solid appeared in both the blank and the exposed electrolyte. A heavy, white, gelatinous film formed on the magnesium surface.
		After Two Weeks	0.8406	3.82×10^{-2} (25°C)	3.71×10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

B. Stability in N,N-Dimethylformamide Solutions.

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm ⁻¹ cm ⁻¹)		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
1. KPF ₆	Li	Before Exposure	0.6446	2.28 x 10 ⁻² (24°C)	2.32 x 10 ⁻² (24°C)	The solution color changed from colorless to orange and a large amount of yellow solid appeared in the solution. The small amount of lithium remaining was covered with a thick yellow film.
		After Two Weeks	5.3802	2.24 x 10 ⁻² (25°C)	2.36 x 10 ⁻² (25°C)	
2. (CH ₃) ₄ NPF ₆ (Tetramethyl- ammonium hexa- fluorophosphate)	Li	Before Exposure	0.6065	1.10 x 10 ⁻² (24°C)	1.11 x 10 ⁻² (24°C)	Light gassing occurred initially. The solution color changed from colorless to light yellow with a great reduction in the volume of the solution. The small amount of lithium remaining was covered with a large amount of white solid. The deterioration of the system made any measurements at the end of the test period impossible.
		After Two Weeks	----	----	1.13 x 10 ⁻² (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

C. Stability in Ethylene Carbonate (80 Wt. %)-
Propylene Carbonate (20 Wt. %) Solutions.

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
1. AlCl_3	Ca	Before Exposure	0.3909	6.03×10^{-3} (23°C)	6.03×10^{-3} (23°C)	The calcium gassed on immersion. Considerable consumption of the calcium occurred. The original light brown solution was colorless after two weeks.
		After Two Weeks	0.0377	4.78×10^{-3} (26°C)	5.07×10^{-3} (26°C)	
	Li	Before Exposure	0.3767	6.03×10^{-3} (23°C)	6.03×10^{-3} (23°C)	The lithium gassed on immersion. After two weeks, some consumption of the lithium had occurred and the remaining lithium was covered with a thin gray film. Both the exposed and unexposed electrolyte changed from light to dark brown.
		After Two Weeks	0.3513	4.79×10^{-3} (26°C)	5.07×10^{-3} (26°C)	
	Mg	Before Exposure	0.2360	6.03×10^{-3} (23°C)	6.03×10^{-3} (23°C)	The magnesium gassed on immersion. There were no other changes in the system.
		After Two Weeks	0.1829	5.13×10^{-3} (26°C)	5.07×10^{-3} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

C. Stability in 80 Wt. % Ethylene Carbonate,
20 Wt. % Propylene Carbonate Solutions. (Continued)

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
2. $(\text{CH}_3)_4\text{NPF}_6$ (Tetramethyl-ammonium hexa-fluorophosphate)	Ca	Before Exposure	0.7964	4.82×10^{-3} (24°C)	4.82×10^{-3} (24°C)	The calcium surface was partly covered by a thin black film.
		After Two Weeks	0.8104	4.87×10^{-3} (25°C)	4.91×10^{-3} (25°C)	
	Li	Before Exposure	0.6661	4.82×10^{-3} (24°C)	4.82×10^{-3} (24°C)	Light gassing occurred on immersion. A black film formed on the lithium surface. A white precipitate formed in solution.
		After Two Weeks	0.8149	4.85×10^{-3} (25°C)	4.91×10^{-3} (25°C)	
3. $(\text{n-C}_3\text{H}_7)_3\text{NHAsF}_6$ (Tri-n-propyl-ammonium hexa-fluoroarsenate)	Mg	Before Exposure	0.4821	4.82×10^{-3} (24°C)	4.82×10^{-3} (24°C)	Approximately 30% of the magnesium surface was covered with a thin layer of black solid.
		After Two Weeks	0.4914	4.90×10^{-3} (25°C)	4.91×10^{-3} (25°C)	
	Li	Before Exposure	0.4307	5.63×10^{-3} (27°C)	5.12×10^{-3} (27°C)	The lithium gassed on immersion. There was no change in the system.
		After Two Weeks	0.4567	1.22×10^{-2} (26°C)	1.22×10^{-2} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

C. Stability in Ethylene Carbonate (80 Wt. %)-
Propylene Carbonate (20 Wt. %). (Continued)

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm ⁻¹ cm ⁻¹)		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
4. $O \begin{matrix} \diagup CH_2CH_2 \\ \diagdown CH_2CH_2 \end{matrix} \begin{matrix} NH_2PF_6 \\ (Morpholinium\ hexa- \\ fluorophosphate) \end{matrix}$	Li	Before Exposure	0.4298	1.18×10^{-2} (23°C)	1.16×10^{-2} (23°C)	Vigorous gassing occurred at the lithium surface upon immersion. At the end of two weeks, most of the lithium had been consumed and a white gelatinous precipi- tate had formed in solution.
		After Two Weeks	0.0896	5.43×10^{-3} (27°C)	1.30×10^{-2} (27°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

D. Stability in N-Nitrosodimethylamine Solutions.

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm ⁻¹ cm ⁻¹)		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
1. AlCl ₃	Ca	Before Exposure	0.3445	9.64×10^{-3} (23°C)	4.64×10^{-3} (23°C)	The calcium became covered with a thick gray film.
		After Two Weeks	0.3622	1.89×10^{-2} (27°C)	1.91×10^{-2} (27°C)	
	Mg	Before Exposure	0.2676	9.64×10^{-3} (23°C)	9.64×10^{-3} (23°C)	The color of the solution changed from yellow-green to orange-brown. The magnesium appeared unchanged.
		After Two Weeks	0.2113	1.81×10^{-2} (27°C)	1.91×10^{-2} (27°C)	
2. KPF ₆	Li	Before Exposure	0.4181	1.72×10^{-2} (24°C)	1.68×10^{-2} (24°C)	The lithium gassed on immersion and became covered with a gray film. There was no other change in the system.
		After Two Weeks	0.5627	1.65×10^{-2} (22°C)	1.67×10^{-2} (22°C)	
	Mg	Before Exposure	0.3116	1.70×10^{-2} (24°C)	1.68×10^{-2} (24°C)	There was no change in the system.
		After Two Weeks	0.3119	1.67×10^{-2} (22°C)	1.67×10^{-2} (22°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

D. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm ⁻¹ cm ⁻¹)		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
3. MgCl ₂	Mg	Before Exposure	0.2831	9.27 x 10 ⁻³ (25°C)	9.37 x 10 ⁻³ (25°C)	The magnesium surface became slightly dull. There was no other change in the system.
		After Two Weeks	0.2899	8.70 x 10 ⁻³ (22°C)	8.58 x 10 ⁻³ (22°C)	
4. (CH ₃) ₄ NPF ₆ (Tetramethyl-ammonium hexa-fluorophosphate)	Ca	Before Exposure	0.3759	5.82 x 10 ⁻⁴ (23°C)	5.82 x 10 ⁻⁴ (23°C)	There was no change in the appearance of the system.
		After Two Weeks	0.3761	9.25 x 10 ⁻⁴ (26°C)	9.03 x 10 ⁻⁴ (26°C)	
	Li	Before Exposure	0.3847	5.82 x 10 ⁻⁴ (23°C)	5.82 x 10 ⁻⁴ (23°C)	A slight amount of light brown solid formed on the lithium surface.
		After Two Weeks	0.4012	8.65 x 10 ⁻⁴ (26°C)	9.03 x 10 ⁻⁴ (26°C)	
	Mg	Before Exposure	0.2565	5.82 x 10 ⁻⁴ (23°C)	5.82 x 10 ⁻⁴ (23°C)	There was no change in the appearance of the system.
		After Two Weeks	0.2625	9.47 x 10 ⁻⁴ (26°C)	9.03 x 10 ⁻⁴ (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS
IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

D. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
5. $(\text{n-C}_3\text{H}_7)_4\text{NPF}_6$ (Tetra-n-propyl-ammonium hexa-fluorophosphate)	Mg	Before Exposure	0.2253	1.78×10^{-2} (23°C)	1.85×10^{-2} (23°C)	The magnesium surface was covered with several black spots at the end of two weeks. The solution changed from yellow to light orange-brown.
		After Two Weeks	0.2444	1.96×10^{-2} (27°C)	1.99×10^{-2} (27°C)	
6. $(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{NPF}_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	Ca	Before Exposure	0.3933	2.13×10^{-2} (23°C)	2.13×10^{-2} (23°C)	The calcium gassed slightly on immersion. The calcium surface became covered with a gray film. A yellow precipitate formed and the solution changed from yellow to orange-brown.
		After Two Weeks	0.5295	2.20×10^{-2} (26°C)	2.20×10^{-2} (26°C)	
	Li	Before Exposure	0.3656	2.13×10^{-2} (23°C)	2.13×10^{-2} (23°C)	The lithium gassed slightly on immersion. The lithium surface became covered with a gray film and a slight amount of orange-brown solid. The solution color changed from yellow to orange-brown.
		After Two Weeks	0.8170	2.19×10^{-2} (26°C)	2.20×10^{-2} (26°C)	
	Mg	Before Exposure	0.2941	2.13×10^{-2} (23°C)	2.13×10^{-2} (23°C)	The magnesium gassed slightly on immersion. The magnesium surface became covered with a gray film. A yellow precipitate formed in solution.
		After Two Weeks	0.4937	2.14×10^{-2} (26°C)	2.20×10^{-2} (26°C)	

TABLE X. DISTILLATION AND TESTING OF SOLVENTS
EMPLOYED IN ELECTROLYTIC SOLUTIONS

	<u>Page</u>
A. Vapor Pressure and Vapor Temperature Ranges During Distillation.	
1. N-Nitrosodimethylamine.....	IV-84
2. Propylene Carbonate.....	IV-84
B. Refractive Indices of Distilled Solvent Fractions at 25°C.	
1. Acetonitrile.....	IV-85
2. N,N-Dimethylformamide.....	IV-85
3. N-Nitrosodimethylamine.....	IV-85
4. Propylene Carbonate.....	IV-86
C. Specific Conductivities of Distilled Solvent Fractions.	
1. Acetonitrile.....	IV-87
2. N,N-Dimethylformamide.....	IV-87
3. N-Nitrosodimethylamine.....	IV-87
4. Propylene Carbonate.....	IV-87

TABLE X. DISTILLATION AND TESTING OF SOLVENTS
EMPLOYED IN ELECTROLYTIC SOLUTIONS

A. Vapor Pressure and Vapor Temperature
Ranges During Distillation.

Fraction (100 ml)	Vapor Pressure (mm)	Vapor Temperature (°C)
1. <u>N-Nitrosodimethylamine.</u>		
1	*	*
2	15	29.5-32.7
3	10-16	32.0-35.0
4	13-16	31.1-34.0
5	13-18	28.0-32.3
6	14-17	28.0-32.0
2. <u>Propylene Carbonate.</u>		
1	*	*
2	14	93
3	13.5	94-94.3
4	14	74.8
5	14	75.1
6	14	76-79.2

* Not recorded since first 100 ml fraction was discarded.

TABLE X. DISTILLATION AND TESTING OF SOLVENTS
EMPLOYED IN ELECTROLYTIC SOLUTIONS (Continued)

B. Refractive Indices of Distilled Solvent Fractions at 25°C.

<u>Fraction</u>	<u>Original</u>	<u>One Week</u>	<u>Two Weeks</u>	<u>Four Weeks</u>	<u>Twelve Weeks</u>
1. <u>Acetonitrile.</u> ($n_D^{16.5} = 1.34596$, Handbook of Chem. & Physics, Chem. Rubber Co., 44th Ed.)					
Undistilled Sample	1.3415	1.3415	1.3420	1.3414	1.3415
1 (Discard)	---	---	---	---	---
2 (100 ml)	1.3414	1.3418	*	*	1.3415
3 (100 ml)	1.3412	1.3416	1.3416	1.3416	1.3415
4 (100 ml)	1.3415	1.3415	1.3415	1.3417	1.3418
5 (12 ml)	1.3416	1.3415	1.3418	1.3416	1.3418
2. <u>N,N-Dimethylformamide.</u> ($n_D^{25} = 1.4269$, DMF, Dupont Product Information Bulletin; $n_D^{25} = 1.4294$, J. Electrochem. Soc., 99, 28, (1952).)					
Undistilled Sample	1.4281	1.4281	1.4280	1.4275	1.4281
1 (Discard)	---	---	---	---	---
2 (100 ml)	1.4279	1.4281	1.4281	1.4283	1.4279
3 (100 ml)	1.4280	1.4282	1.4281	1.4283	1.4281
4 (100 ml)	1.4279	1.4282	1.4281	1.4281	1.4281
5 (100 ml)	1.4281	1.4281	1.4281	1.4280	1.4282
6 (100 ml)	1.4279	1.4280	1.4281	1.4282	1.4280
3. <u>N-Nitrosodimethylamine.</u> ($n_D^{18.4} = 1.43743$, Handbook of Chem. & Physics, Chem. Rubber Co., 44th Ed.)					
Undistilled Sample	1.4339	1.4339	1.4340	1.4340	
1 (Discard)	---	---	---	---	
2 (100 ml)	**	1.4344	1.4344	1.4345	
3 (100 ml)	**	1.4344	1.4344	1.4346	
4 (100 ml)	**	1.4343	1.4345	1.4345	
5 (100 ml)	**	1.4344	1.4344	1.4345	
6 (100 ml)	**	1.4345	1.4344	1.4346	

* Field of refractometer was indistinct. Values were ca. 1.3465.

** Not measured.

TABLE X. DISTILLATION AND TESTING OF SOLVENTS
EMPLOYED IN ELECTROLYTIC SOLUTIONS (Continued)

B. Refractive Indices of Distilled Solvent Fractions at 25°C. (Continued)

<u>Fraction</u>	<u>Original</u>	<u>One Week</u>	<u>Two Weeks</u>	<u>Four Weeks</u>	<u>Twelve Weeks</u>
4. <u>Propylene Carbonate.</u>					
Undistilled Sample	1.4194	1.4177	1.4196	1.4193	1.4195
1 (Discard)	---	---	---	---	---
2 (100 ml)	1.4197	1.4190	1.4194	1.4199	1.4199
3 (100 ml)	1.4195	1.4198	1.4193	1.4196	1.4200
4 (100 ml)	1.4198	1.4168	1.4176	1.4195	1.4199
5 (100 ml)	1.4198	1.4162	1.4190	1.4196	1.4198
6 (100 ml)	1.4198	1.4163	1.4179	1.4192	1.4199

TABLE X. DISTILLATION AND TESTING OF SOLVENTS
EMPLOYED IN ELECTROLYTIC SOLUTIONS (Continued)

C. Specific Conductivities of Distilled Solvent Fractions.

Fraction	Original	One Week	Two Weeks	Four Weeks	Twelve Weeks
1. Acetonitrile. ($L = 5.9 \times 10^{-8}$ ohm $^{-1}$ cm $^{-1}$, J. Electrochem. Soc., 112, 104, (1965).					
Undistilled Sample	2.13×10^{-6}	2.62×10^{-6}	3.04×10^{-6}	4.78×10^{-6}	4.62×10^{-6}
1 (Discard)	---	---	---	---	---
2 (100 ml)	7.25×10^{-7}	3.22×10^{-6}	4.44×10^{-6}	6.84×10^{-6}	8.00×10^{-6}
3 (100 ml)	8.58×10^{-7}	1.69×10^{-6}	2.94×10^{-6}	4.98×10^{-6}	7.83×10^{-6}
4 (100 ml)	3.10×10^{-7}	1.28×10^{-6}	2.94×10^{-6}	5.37×10^{-6}	8.56×10^{-6}
5 (12 ml)*	---	---	---	---	---
2. N,N-Dimethylformamide. ($L = 0.6-2.0 \times 10^{-7}$ ohm $^{-1}$ cm $^{-1}$, J. Phys. Chem., 59, 16-17, (1955).					
Undistilled Sample	1.30×10^{-6}	1.33×10^{-6}	3.24×10^{-6}	5.61×10^{-6}	2.89×10^{-5}
1 (Discard)	---	---	---	---	---
2 (100 ml)	1.65×10^{-6}	5.91×10^{-6}	1.96×10^{-5}	2.50×10^{-5}	3.08×10^{-5}
3 (100 ml)	6.66×10^{-7}	1.78×10^{-6}	3.66×10^{-6}	4.23×10^{-6}	7.27×10^{-6}
4 (100 ml)	5.34×10^{-6}	8.25×10^{-6}	9.15×10^{-6}	1.07×10^{-5}	1.52×10^{-5}
5 (100 ml)	4.46×10^{-6}	7.95×10^{-6}	8.45×10^{-6}	1.00×10^{-5}	1.16×10^{-5}
6 (100 ml)	7.43×10^{-7}	2.82×10^{-6}	3.69×10^{-6}	4.20×10^{-6}	6.22×10^{-6}
3. N-Nitrosodimethylamine.					
Undistilled Sample	2.64×10^{-5}	9.95×10^{-6}	1.34×10^{-5}	1.78×10^{-5}	
1 (Discard)	---	---	---	---	
2 (100 ml)	**	1.25×10^{-5}	7.59×10^{-5}	7.90×10^{-5}	
3 (100 ml)	**	2.18×10^{-6}	9.3×10^{-6}	6.88×10^{-5}	
4 (100 ml)	**	3.41×10^{-6}	1.05×10^{-5}	5.28×10^{-5}	
5 (100 ml)	**	3.34×10^{-6}	2.96×10^{-5}	6.53×10^{-5}	
6 (100 ml)	**	1.05×10^{-5}	5.15×10^{-5}	8.16×10^{-5}	
4. Propylene Carbonate.					
Undistilled Sample	1.37×10^{-5}	1.37×10^{-5}	1.38×10^{-5}	1.45×10^{-5}	1.39×10^{-5}
1 (Discard)	---	---	---	---	---
2 (100 ml)	6.97×10^{-8}	5.85×10^{-7}	1.07×10^{-6}	1.22×10^{-6}	1.42×10^{-6}
3 (100 ml)	4.01×10^{-8}	4.20×10^{-7}	4.64×10^{-7}	7.43×10^{-7}	1.01×10^{-6}
4 (100 ml)	6.06×10^{-8}	8.30×10^{-8}	2.32×10^{-7}	3.50×10^{-7}	7.93×10^{-7}
5 (100 ml)	9.71×10^{-8}	1.22×10^{-7}	2.30×10^{-7}	3.78×10^{-6}	1.15×10^{-6}
6 (100 ml)	6.37×10^{-8}	1.02×10^{-7}	2.22×10^{-7}	3.02×10^{-6}	1.05×10^{-6}

* Specific conductivity could not be measured because of small volume.

** Not measured.

TABLE XI. ELECTROCHEMICAL HALF-CELL SCREENING
OF ANODES IN PURIFIED SOLVENTS

		Page
<u>Lithium Anode Systems.</u>		IV-89
<u>Solvent</u>	<u>Solute</u>	
1. Dimethylformamide (DMF) (Vacuum Distilled)	N-Phenyl-N,N,N-trimethylammonium- hexafluorophosphate - $(C_6H_5)(CH_3)_3NPF_6$	
2. DMF (Distilled at Atmospheric Pressure)	N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate	
3. DMF (Not Distilled)	N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate	
4. DMF (Vacuum Distilled)	Morpholinium hexafluorophosphate - $O \begin{array}{c} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{array} \text{NH}_2\text{PF}_6$	
5. DMF (Not Distilled)	Morpholinium hexafluorophosphate	
6. N-Nitrosodimethylamine (NDA) (Distilled)	N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate	
7. NDA (Not Distilled)	N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate	

Each system is classified under the current density at which the anode exhibited less than 50% polarization from the initial open circuit potential.

All electrolytes are 1 molal in concentration.

TABLE XI. ELECTROCHEMICAL HALF-CELL SCREENING
OF ANODES IN PURIFIED SOLVENTS

Lithium Anode Systems.

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute	Reference Electrode	Counter Electrode	Initial	Various Current Densities	Current Density (ma/cm ²)	Initial	Final	
1. DMF (Distilled) (Vacuum Distilled)	*	Ag/AgCl	Ag/AgCl	-3.13	-3.13 -3.14 -3.16 -3.17	0.1 1 10 100	-3.11 -3.01 -2.67 -1.90	-3.12 -3.04 -2.85 -2.05	The DMF used was fractionally distilled at low pressures and stored in an argon atmosphere until used. The lithium began gassing during the 10 ma discharge and continued to do so. During the 100 ma discharge the lithium surface became covered with a black film and deterioration of the counter electrode occurred. There was no change in the appearance of the reference electrode or the electrolyte. System capable of sustaining 100 ma/cm ² .
2. DMF (Distilled) at Atmospheric Pressure)	*	Ag/AgCl	Ag/AgCl	-3.08	-3.10 -3.12 -3.16 -3.17	0.1 1 10 100	-3.06 -2.90 -2.68 -1.90	-3.07 -2.96 -2.84 -2.06	The DMF used was fractionally distilled at atmospheric pressure and stored in an argon atmosphere until used. Slight gassing began at the lithium anode during the 10 ma discharge. At 100 ma, the gassing rate was moderate and the lithium blackened. Slight gassing continued on open circuit. The counter electrode deteriorated slightly. No change in the appearance of the solution or the reference electrode. System capable of sustaining 100 ma/cm ² .

* N-phenyl N,N,N-trimethylammonium hexafluorophosphate - (C₆H₅)(CH₃)₃NPF₆

TABLE XI. ELECTROCHEMICAL HALF-CELL SCREENING
OF ANODES IN PURIFIED SOLVENTS (Continued)

Lithium Anode Systems. (Continued)

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute						Initial	Final	
DMF (Not Distilled)	*	Ag/AgCl	Ag/AgCl	-3.12	-3.18 -3.19 -3.20 -3.18	0.1 1 10 100	-3.12 -3.03 -2.77 -1.65	-2.17 -3.06 -2.85 -1.77	The lithium anode began gassing moderately after four minutes of the 100 ma discharge and turned black. Slight gassing continued on open circuit. The counter electrode deteriorated slightly. No change in the appearance of the solution or the reference electrode. System capable of sustaining 100 ma/cm ² .

* N-phenyl N,N,N-trimethylammonium hexafluorophosphate - (C₆H₅)(CH₃)₃NPF₆

TABLE XI. ELECTROCHEMICAL HALF-CELL SCREENING
OF ANODES IN PURIFIED SOLVENTS (Continued)

Lithium Anode Systems. (Continued)

Electrolyte		Counter Electrode	Reference Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute						Initial	Final	
4. DMF (Vacuum Distilled)	*	Ag/AgCl	Ag/AgCl	-3.16	-3.14 -3.16 -3.12 -3.15	0.1 1 10 100**	-3.15 -3.13 -2.80 -2.00	-3.14 -3.12 -2.67 -1.50	Upon immersion the lithium surface turned black and gassing occurred. Considerable consumption of the lithium occurred and the lithium electrode was replaced for the 10 ma discharge. A large amount of gray-green solid formed in solution. The solution changed from colorless to orange-brown. The counter electrode deteriorated. There was no change in the reference electrode. The system was capable of sustaining 10 ma/cm ² .
5. DMF (Not Distilled)	*	Ag/AgCl	Ag/AgCl	-3.20	-3.25 -3.22 -3.18 -3.22	0.1 1 10 100	-3.24 -3.25 -3.04 -1.94	-3.28 -3.23 -3.00 -1.72	Vigorous gassing at the lithium electrode on open circuit and during discharge. The lithium was gradually consumed and a precipitate formed in solution. The appearance of the reference and counter electrodes was unchanged. The system was capable of sustaining 100 ma/cm ² .

* Morpholinium hexafluorophosphate - $O \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}_2\text{PF}_6$

** Voltages during this discharge fluctuated over a ± 0.2 volt range.

TABLE XI. ELECTROCHEMICAL HALF-CELL SCREENING
OF ANODES IN PURIFIED SOLVENTS (Continued)

Lithium Anode Systems. (Continued)

Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm ²)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
Solvent	Solute						Initial	Final	
6. NDA (Distilled)	*	Ag/AgCl	Ag/AgCl	-2.67	-2.76	0.1	-2.68	-2.75	The lithium anode gassed continuously. During the 0.1 ma/cm ² discharge a gray solid began to form on the lithium. At the end of the discharges the counter electrode had turned black but whitened on standing. System capable of sustaining 100 ma/cm ² .
					-2.76	1	-2.72	-2.73	
					-2.78	10	-2.53	-2.57	
					-2.83	100	-1.35	-1.67	
7. NDA (Not Distilled)	*	Ag/AgCl	Ag/AgCl	-3.42	-3.20	0.1	-3.35	-3.10	Solution became dark in color. No gassing was apparent. Lithium became somewhat darker in appearance. System capable of sustaining 10 ma/cm ² .
					-3.05	1	-2.84	-2.78	
					-3.05	10	-2.20	-2.18	
					-2.95	100	-1.20	-0.8	

* N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate - (C₆H₅)(CH₃)₃NPF₆